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1901

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# Journal of Analytical Chemistry.

Volume IV, 1890.

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EDITED BY EDWARD HART, Ph. D.,  
PROFESSOR OF ANALYTICAL CHEMISTRY, LAFAYETTE COLLEGE.

ASSOCIATE EDITOR:

P. W. SHIMER, M. E. . . . . IRON AND STEEL

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WITH THE ASSISTANCE OF THE FOLLOWING SPECIALISTS:

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ABSTRACTORS:

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C. W. MARSH, Ph. D.	A. H. WELLES, B. S.
J. E. WHITFIELD.	A. A. BLAIR.

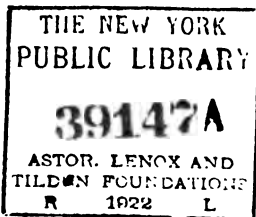
EASTON, PA.

PUBLISHED BY THE EDITORS.

G. W. ESCHENBACH, BOOK AND COMMERCIAL PRINTER.  
1890.

RECEIVED  
JAN 10 1891  
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# Journal of Analytical Chemistry.

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## REPORT OF THE COMMITTEE ON METHODS OF SUGAR ANALYSIS OF THE LOUISIANA SUGAR CHEMISTS' ASSOCIATION.\*

COMPRISING  
METHODS OF SUGAR ANALYSIS AND INSTRUCTIONS FOR THE  
GUIDANCE OF SUGAR CHEMISTS.

NOTE.—In compliance with a resolution adopted at a meeting of the Sugar Chemists' Association on October 10th, this pamphlet has been prepared for the guidance and instruction of chemists engaged in the chemical control of sugar houses. As many of the analysts whom this publication will reach are just entering upon, or have only a limited experience in, the laboratory work of the sugar house, the instructions and directions, herein given, partake more of an elementary and detailed character than would otherwise be the case. On the other hand, the limited time at the disposal of the committee has precluded the treatment of certain portions of the subject in extenso.

B. B. ROSS,  
MAURICE BIRD,  
*Of the Committee on Methods of Analysis.*

### APPARATUS, CHEMICALS AND CHEMICAL REAGENTS ESSENTIAL TO THE EQUIPMENT OF A SUGAR HOUSE LABORATORY.

*Apparatus.*—Polariscope, with observation tubes, polariscope lamp, funnels, beakers, sugar flasks graduated 100 cc. to 110 cc. and smaller size flasks graduated to 50 cc. and 55 cc.; burettes (with  $\frac{1}{10}$  cc. graduations) and burette support, casseroles, porcelain evaporating dishes, water bath, retort stand, centigrade thermometer, set of Brix hydrometers with cylinder, liter flask, wash bottle, pipettes, glass tubing, filter paper, litmus test paper, pair of balances, set of weights, German silver sugar dish with counterpoise and normal sucrose weights, an alcohol lamp for heating purposes, or a Bunsen burner if a gas supply can be obtained.

*Chemicals and Reagents.*—Lead acetate, litharge, copper sulphate, Rochelle salt, caustic soda, potassium ferrocyanide, anhydrous glucose, C.P. acetic acid, hydrochloric acid, sodium carbon-

\*Reprinted from a pamphlet issued by the Louisiana Bureau of Agriculture.

ate, boneblack, finely cut asbestos, solution basic lead acetate, Fehling's copper solution.

*Selection and Adjustment of Instruments, Apparatus, etc.*—For all the ordinary analytical work in the sugar house, the polariscopes with the horizontal sugar scale of 100 parts are to be preferred to those in which the circular scale of degrees is employed, and in which the exact angle of rotation, and not the direct per cent of sugar is read. The instruments of this latter description are invariably constructed *a penombre* and require the use of a monochromatic (sodium) light in a dark room, and a consequent expenditure of more time and manipulation than in corresponding determinations with saccharimeters adapted to ordinary lamp light. Of the various makes and styles of instruments of the last named class, a large proportion have the same normal sucrose weight of 26.048 grams, with a normal length of 200 millimeters for observation tubes. The shadow polariscope, adapted to white light, is the form of instrument more generally used at present, but the color instruments, provided with a regulator for changing the tints of the field of the instruments, is frequently preferred by those who experience no difficulty in detecting slight shades of difference in color. The Schmidt & Haensch shadow instrument, with double compensating wedges, and with a capacity for 400 mm. tubes is to be especially commended for its ease of manipulation and the accuracy of results, it being possible to check each individual reading four times by means of the duplicate scales, while any incidental errors are reduced one-half by the use of the 400 mm. tubes. The Soleil-Ventzke and Scheibler instruments, and most especially, the shadow instrument of the latter make, are extremely well adapted to the ordinary work of the sugar house laboratory and in the hands of a careful operator give results whose accuracy may be confidently relied upon.

In the adjustment of polariscopes, care should be taken that the sugar used in the preparation of the normal sucrose solution is of absolute purity. Either pure white rock candy, in well defined crystals, or the best loaf sugar, extracted with 85 per cent. alcohol and well dried at a temperature slightly below 100° C., should be used. The rock candy should be thoroughly pulverized and pressed between sheets of blotting or filter paper previous to

weighing, or if the atmosphere is heavily charged with moisture, it will be best to dry it at a temperature just below the boiling point of water.

The normal weight, 26.048 grams, of sucrose is weighed out, dissolved in pure distilled water, and diluted to a bulk of 100 cc. The gauging of the sucrose solution should be performed as nearly as possible at 17.5° C., as, in sugar analysis, that is the standard temperature for measurements and polariscope readings.

For ascertaining the correctness of the zero point of the instrument, the polariscope tube is filled with pure distilled water, and having obtained a uniform tint or shade in the field of the polariscope, the variation in the position of the two zeros is corrected by means of the key applied near the left hand extremity of the vernier scale. Having made this adjustment, the normal sucrose solution should give a reading of 100 if the analyzer and polarizer are in a right position with regard to each other. If, however, no uniformity of shade or tint on both sides of the centre line, is observed for any position of the movable quartz wedge, the analyzer and polarizer are out of adjustment with reference to each other. In order to effect a correct adjustment of the parts, the movable quartz wedge must be taken out by turning the milled head screw underneath until it can be easily slipped out; the stationary quartz wedge is next displaced by removing the screws which hold it in position and which are usually found almost underneath the screws which hold in place the apparatus for reading the scale. The compensation quartz plate is next removed by opening the cover of the chamber for the reception of the observation tubes and unscrewing the plate at the end nearest the observer. The cover having been closed, an observation is taken, and the position of the analyzer is corrected by applying the polariscope key to the screw head on the right of the instrument, and just in the rear of the compensation plates. The key is turned until there is a uniformity of shade on both sides of the vertical center line of the field of the apparatus. The compensation wedges and plates having been replaced, a reading with an empty tube is made and any deviation in the position of the two zeros is corrected as before explained.

The linear measure of all polariscope tubes should be carefully

taken, as any variation from the standard length will cause directly proportional errors in results. This measurement, from end to end, should be effected by means of a pair of dividers or calipers, the divergence of the points of the instrument, when applied to a finely graduated metric scale, giving accurately the length of the tube. Tubes showing a perceptible variation from the normal length should be rejected, or else, all readings made in them should be corrected in direct proportion to the error in length. Where instruments have a capacity for 400 mm. tubes, the long tubes should be invariably used for juices and syrups, when practicable, and the 100 mm. tubes should only be employed in polarization of dark or difficult decolorizable solutions, as decrease in length of polariscope tubes is attended with a proportional increase in errors. For double polarizations, it is far preferable to use those tubes provided with a central tubulure, at right angles to their length, for the insertion of a thermometer and the recording of temperature at the instant of reading. It is also preferred that the tubes be one-tenth longer than those used for direct readings, in order to compensate for the dilution of the solution. The Scheibler instruments, generally employed, however, will not accommodate tubes of a greater length than 200 mm.

In filling tubes with solutions for analysis, it is always best to first rinse them out with the juice or sugar solution under examination, and afterward fill the tube (holding it in a vertical position) until the liquid reaches the upper end and assumes a convex surface; the glass disk is then slipped on horizontally, and the screw cap is adjusted and tightened, absence of bubbles being thus almost invariably insured. The glass covers of the tube should, after filling, also be wiped free of any particles or drops of liquid, silk, chamois skin or filter paper being used for this purpose, instead of cotton or linen, small particles of which latter substances frequently attach themselves to the glasses. The tubes should be emptied of their contents as soon as the observation is completed, the retention in metallic tubes, of solutions, inverted by means of acid, being especially injurious.

The lamp best adapted to polariscope work is of the "German Student" pattern, supplied with a clay cylinder with side aperture, oil being preferred to gas as an illuminating agent. The end of

the instrument should not be placed nearer than from 2 to 2½ inches from the source of light, as the heat from the lamp tends to affect the cement used in holding the prisms in position.

In order to test the correctness of the calibration of measuring flasks used in the various operations herein described, it will be necessary to first dry the empty flask and then weigh it. Distilled water (whose specific gravity, corrected for temperature, has just been determined) is run into the flask until the lower edge of the meniscus at the surface of the liquid is on a line with the mark on the neck of the flask. The flask and contents are then weighed, the increase in weight divided by the specific gravity of water at that temperature, giving the correct capacity of the flask in centimeters.

*Determination of Sucrose.*—In weighing, the balances used need only be sensitive to within 10 milligrams, as that amount of variation in the weight of a sample would scarce be appreciable in the readings of the polariscope. Transfer, by means of a pipette, to the tared German silver sugar dish, the normal weight of the juice or syrup to be analyzed, a spatula or other device being used in case the sample is not of a liquid consistency.

In the case of juices and thin syrups, the contents of the dish are at once washed into the 100 cc. flask; sugars, *masse cuite*, heavy molasses, etc., however, are best dissolved in the dish previous to being transferred.

The solution in the flask is made up to 80 or 90 cc. and the least amount of basic lead acetate solution, sufficient to decolorize the contents, is added. The solution is then made up to the 100 cc. mark and thoroughly shaken before filtering. In case much foaming and bubbling takes place, rendering gauging difficult, the addition of a few drops of ether is found advantageous. The solution is then poured upon a dry filter and the filtrate is collected in a dry beaker, the first portions to pass through being rejected. If it is found impossible to obtain a perfectly clear filtrate, it may be necessary to decolorize with dry, powdered boneblack, either mixed with liquid itself or placed upon the filter. Should it be desired to remove the excess of lead in the solution before polarizing, it can be precipitated out

before filtering, by means of sodium carbonate or sulphate (preferably the latter). The tube is filled with the clear solution as before described, and the process of reading the instrument is conducted as usual.

*Double Polarization.*—Fifty cc. of the decolorized solution used in the direct polarization test is placed in a sugar flask, graduated to 50 to 55 cc., and hydrochloric acid of sp. gr. 1.18–1.20 is added until the liquid reaches the 55 cc. mark, the contents being well shaken. The flask and contents are then heated in a water bath at a temperature of 68°–75° C. for about fifteen minutes. It is then allowed to cool, freed from the precipitate of lead chloride by filtration, the filtered solution being transferred to a tube of the form previously referred to as being especially adapted to the reading of invert solutions. The reading of the solution to the left is noted, and at the same time its temperature is carefully taken by means of a thermometer inserted in the central tubulure of the tube. In calculating the true per cent. of sucrose from the data thus obtained, instead of Clerget's original constant of 144, the revised figure of 142.4 should be used, as the committee's experiments show conclusively that 26.048 grams of sucrose, inverted and made up to 100 cc., gives a reading to the left of 42.4 at 0° C. The correct expression of the formula used in the calculations will then be  $R = \frac{100 S}{142.4 - \frac{1}{2} T}$ , in which S = the sum of the right and left-handed readings of the solution; T = the temperature of the solution at the instant the left-handed reading is taken, while R is equal to the corrected per cent of sucrose. Where it is preferred, the simple proportion  $142.4 - \frac{1}{2} T : 100 :: S : R$  — can be used.

In double polarization tests, the readings of the invert solutions should invariably be conducted at, as nearly as possible, the same temperatures as the direct readings.

*Specific Gravity and Density.*—Density of juices, syrups, etc., is most conveniently determined by means of Beaume's or Brix's hydrometer or areometer, preferably with the latter, as the graduations of the scale give close approximations to the percentages of total solids. The Brix spindle should be graduated to tenths, the divisions of the scale being of sufficient length to enable the analyst to note exactly the point to which the stem sinks in the

liquid. It is therefore desirable, for accuracy, that the range of degrees recorded by each individual spindle be as limited as possible, this end being best secured by the employment of sets, consisting of not less than three spindles. The solutions should be, as nearly as possible, of the same temperature as the air at the time of reading, and if the variation from the standard temperature of the graduation of the spindle, amounts to more than  $1^{\circ}$  C., compensation therefor must be made by reference to the table of corrections for temperature on page 114, Tucker's Sugar Analysis.

Care should be observed, in taking the density of a juice, to allow it to stand in the cylinder until all air bubbles have escaped, before reading the spindle. When it is desired to accurately determine the specific gravity of the sample, a specific gravity bottle or picnometer, of 50 cc. capacity, is employed, and the weight of the amount required to fill the bottle at  $15.5^{\circ}$  C., divided by 50, gives its correct specific gravity. When the temperature varies from the standard temperature for specific gravities, the weight of the juice must be compared with an equal volume of water, weighed at the same temperature.

*Total Solids.*—The per cent. of total solids can be approximately ascertained directly from the reading of the Brix hydrometer, or knowing the reading of the Beaume spindle, or the specific gravity of the sample, by reference to the table on pages 116–118 Tucker's Sugar Analysis, the desired percentage can be obtained.

In order to accurately estimate the proportion of total solids in a juice or syrup, from one to three grams (according to the density of the liquid) are run into a porcelain or glass dish, containing about two grams of finely powdered, ignited silica. The whole is then placed on a water bath and heated until the contents are apparently dry, after which it is transferred to an air bath and dried to a constant weight at not exceeding  $110^{\circ}$  C. The weight of the dish and silica subtracted from weight of dish and contents after drying gives total solids.

Total solids may also be determined by Dr. Wiley's method of saturating a dried and weighed piece of filter paper (about 12 by



2 inches in size) with the sample of juice or molasses, and drying at 100° and reweighing.

*Determination of Glucose.*—In the analysis of juices, 10 grams of the sample are weighed out, transferred to a graduated flask made up to 100 cc.; in estimations of glucose in molasses and syrups, 5 grams are weighed out and diluted to 500 or 1000 cc., according as the proportion of glucose present is relatively small or large.

It is best that the diluted solution contain not more than 2 milligrams of glucose to the centimeter of liquid. Ten cubic centimeters of Fehling's solution are next run into a casserole from a burette and three or four times its bulk of water added; it is then placed over a flame and brought to a brisk boil, care being taken to observe whether or not any of the copper is precipitated as sub-oxide. If no precipitation is noticed, a few cubic centimeters of the solution under examination are added from a burette and the contents of the casserole are again boiled, stirred well, removed from the lamp and the precipitate allowed to subside. The process is thus continued, the sugar solution being run in at short intervals, and in small quantities at a time, the liquid in the casserole being boiled and allowed to settle each time. When the blue tint has almost disappeared from the liquid, and the dull red of the precipitate has changed to a scarlet, the solution is added very cautiously, stirring and settling as before. When the precipitate subsides readily, and the supernatant liquid becomes clear and almost colorless, a test is made to ascertain whether or not all the copper is precipitated. A few drops of the liquid, when filtered and placed on a porcelain casserole cover or crucible top, will, when acidulated with acetic acid, give a reddish brown precipitate with potassium ferrocyanide, if any copper remains in solution. The filtration of a small portion of the solution for testing, is best effected by means of Wiley's tubes—easily prepared by making a flange on one end of a piece of glass tubing, about  $\frac{3}{8}$  inch diameter and 5 or 6 inches in length, and covering the flanged end with a small piece of muslin. An asbestos pulp is next prepared by boiling finely chipped asbestos with water, and an amount sufficient to cover the muslin is then

sucked up on the closed end of the tube. In testing the supernatant liquid in the casserole, a very small portion is sucked through the asbestos filter, the tube being at once inverted in order to drop the contents on the porcelain surface. Operators should be careful to remove as little of the solution as possible at one time from the casserole, and to only commence testing the solution when it is apparent to the eye that the liquid is almost completely decolorized. Frequent tests and the use of large quantities of the solution in making tests, tends to give results too high.

Instead of employing Wiley's tubes as explained above, a piece of tubing about the same dimensions is drawn out to a small bore at a point about an inch from the end; a small plug of dry asbestos is now inserted in the short section of the tube next to the constriction, and the tube is ready for use in the manner before described.

In calculating results the following proportion can be used; no. cc. of solution required to precipitate the copper in 10 cc. Fehling's solution: amount in grams of glucose equivalent to 10 cc. Fehling's solution :: 1000 :  $x$ . If 10 grams of the sample diluted to 10 cc., were used,  $x$  will give exact percentage of invert sugars in sample analyzed.

*Determination of Sucrose by Inversion.*—In analysis of syrups, molasses, etc., 2 to 5 grams of the samples are weighed out, washed into a flask, and diluted to 200 or 300 cc.; 5 cc. strong hydrochloric acid is then added, and the flask and contents are heated in a water bath for fifteen minutes at a temperature of 65°–75° C. The solution is then neutralized with sodium carbonate, made up to a volume of one liter and invert sugar is determined as before described. The total invert sugar minus glucose previously determined, gives amount of glucose equivalent to sucrose present; this amount multiplied by .95 gives the amount of sucrose contained as determined by inversion. When it is desired to decolorize juices previous to determining glucose, or to determine glucose in a solution prepared for polarization, the excess of lead used in clarifying should be precipitated by means of pulverized sodium carbonate, and the solution diluted to the requisite volume, and filtered before making the estimation.

The essential data to be given in stating the results of an analysis of juice are as follows:

Specific gravity.  
Density, Degrees Brix or Beaume.  
Total solids.  
Sucrose.  
Glucose.  
Solids not sugars.  
Co-efficient of purity.  
Glucose ratio.

The proportion of solids not sugars is ascertained by subtracting the sum of the per cents of sucrose and glucose from per cent. of total solids. The co-efficient of purity is obtained by dividing the per cent. of sucrose by per cent. of total solids and multiplying by 100. The glucose ratio, or ratio of glucose to sucrose, is obtained by dividing per cent. glucose by per cent. sucrose and multiplying by 100. The per cent. of available sugar\* is ascertained by subtracting  $1\frac{1}{2}$  times the per cent. of glucose from the per cent. of sucrose. "Pounds of available sugar per ton of cane" is obtained by multiplying 2000 by the per cent. of available sugar, and the product by the per cent. of extraction. The per cent. of extraction is obtained by dividing weight of juice by weight of cane and multiplying by 100.

#### REAGENTS.

*Preparation of Basic Lead Acetate.*—Weigh out about 220 grams normal lead acetate, and 130 grams of litharge; boil with 700 to 800 cc. water for about one-half hour, stirring well to promote solution and prevent bumping. Cool, dilute to one liter, and siphon or filter off the clear supernatant liquid. Instead of the above proportions of lead acetate and oxide, 350 grams of lead subacetate (basic acetate), dissolved in water and diluted to 1000 cc., may be employed.

*Fehling's Solution.*—Weigh out accurately 34.640 grams of crystallized copper sulphate, C. P., dissolve in about 200 cc. water by the aid of a gentle heat and allow to cool. Also weigh out 180 grams crystallized sodium potassium tartrate (Rochelle

\*NOTE.—This is purely empirical, and practical factory results have, in many instances, demonstrated that available sugar estimates are thus rendered too low.

salt) and 70 grams of caustic soda; dissolve in about 500 or 600 cc. water, heating gently; cool, and pour into it slowly the copper sulphate solution, stirring the mixture well. Transfer to a liter flask and dilute to a bulk of 1000 cc. Preserve in a tightly stoppered bottle in a dark place. Solutions which allow the formation of a precipitate of copper sub-oxide on standing, or when diluted with water and boiled, should be rejected as untrustworthy.

*Standard Glucose Solution.*—The glucose solution used in standardizing Fehling's copper solution is best prepared by dissolving 2 grams of C. P. anhydrous glucose in distilled water, and diluting to a volume of one liter, thus giving a solution containing 2 milligrams of glucose per cubic centimeter.

In order to determine the true strength of the copper solution, 10 cc. are run into a casserole from a burette and are diluted to three or four times that bulk with water. The liquid is then heated to boiling, and the glucose solution run in gradually until the precipitation of the copper is complete, the end point of the reaction being determined as previously described under the head of glucose estimations. The number of cc. of the glucose solution taken, multiplied by 2, will give the number of milligrams of glucose required to precipitate the copper in 10 cc. of the Fehling's solution.

The potassium ferrocyanide solution is prepared by dissolving 80 grams in water and diluting to a bulk of one liter.

The dilute acetic acid used should be about 20 per cent. to 30 per cent. strength.

The hydrochloric acid used in inversion should have a specific gravity of 1.18–1.20.

*Determination of Ash.*—Two to three grams of the sample is ignited at a red heat in a weighed platinum or nickel dish until destruction of organic matter is complete.

The sample, previous to incineration in a platinum dish, may be treated with about one cubic centimeter of concentrated sulphuric acid, the heat being applied gradually at first, and then to full redness. One-tenth must be deducted from the weight of the ash thus obtained, on account of the increase in weight caused

by the combination of the sulphuric acid with some of the ash constituents.

*Calculation of Losses from Inversion.*—In calculating losses from inversion, the formula given by Dr. Stubbs, in the *Louisiana Planter* of March 30, 1889, is recommended, as by its use the amount of sucrose inverted can be estimated very closely, even where the weight of the juice only, as it comes from the mill, is known. The only data required in this determination is the weight of juice, and the per cents of sucrose and glucose in the juice, and in the products of the different stages of the manufacture. The total amount of inversion, or the amount of sucrose inverted in any single operation, can be readily determined by the application of the formula as here given :

Let  $s$  = per cent. sucrose in raw juice.

$g$  = per cent. glucose in raw juice.

$s'$  = per cent. of sucrose in clarified juice, syrup, or masse cuite.

$g'$  = per cent. of glucose in clarified juice, syrup, or masse cuite.

$w$  = weight of raw juice.

Let  $x$  = sucrose inverted between raw juice and clarified juice, syrup, or masse cuite, as the case may be.

Then  $\frac{100}{95}x$  = glucose gained at same time, as 95 parts of sucrose on inversion yield 100 parts of glucose.

Then  $ws - x$  = sucrose in clarified juice, syrup, or masse cuite.

And  $wg + \frac{100}{95}x$  = glucose in same.

But in the clarified juice, syrup, or masse cuite, the total sucrose and glucose are to each other as  $s'$  is to  $g'$ ; therefore,

$$ws - x : wg + \frac{100}{95}x :: s' : g'; \text{ from which } x = \frac{95 w (sg' - s'g)}{95 g' + 100}$$

This method of calculation can even be applied to the molasses by subtracting from  $ws$ , before substitution, the amount of pure sugar obtained by weighing and polarizing as it comes from the centrifugal.

*Sampling.*—As the chief object in taking samples is to obtain small fractional portions of the juice and the products of the various processes of the sugar house, representing, as nearly as possible, in composition, the whole, care should be observed to conduct the sampling in such a manner, as regards time and quantity, as to secure analytical results of as comprehensive character as possible. In sampling juice, small quantities should be taken

from the trough at equal short intervals, and thoroughly mixed, the mixture thus obtained being fairly representative of the juice extracted during the time occupied in taking the samples. In drawing samples of juice or syrup from tanks, the contents should be well mixed by stirring before taking out the desired quantity for analysis; if several of these tanks, however, are to furnish a sample for a single analysis, quantities proportional to the size of each tank should be taken and the whole well mixed. In sampling juice from clarifiers, a mixture of equal quantities taken from several successive fillings of the clarifier, will represent fairly well the whole bulk of juice sampled.

It is recommended that samples for analysis be taken as follows :

Raw juice—a sample at least every six hours.

Sulphured juice—sample taken after heating; sampling before heating is considered unnecessary; tests should be made at same intervals as for raw juice.

Clarified juice—sample taken at same intervals as for raw juice.

Syrup—every tank should be sampled.

Sampling of *masse cuite* is to be condemned, as it has been found well nigh impossible to obtain samples homogeneous in character and representative of the whole. The true percentages of sucrose and glucose contained in the *masse cuite* can be closely determined by analyzing and weighing the sugar and molasses produced, and combining the results as follows :

Let  $w$  = weight of sugar.

$w'$  = weight of molasses.

$s$  = per cent. sucrose in the sugar.

$g$  = per cent. glucose in the sugar.

$s'$  = per cent. sucrose in molasses.

$g'$  = per cent. glucose in molasses.

Then, by combining these terms in formula, we have the per cent of sucrose in the *masse cuite* =  $100 \frac{(ws + w's')}{w + w'}$  and per cent. of glucose =  $100 \frac{(wg + w'g')}{w + w'}$

The control of diffusion work differs from that of mill work, in that, in addition to the sampling and analysis of the extracted juice, the sugar content of both the fresh and exhausted cane must also be determined.

The fresh chips are passed through an ordinary hand mill, and the analysis of the juice is conducted as usual. The per cent. of

sucrose in the juice, multiplied by the estimated average per cent. of juice in cane and divided by 100, gives per cent. of sucrose in cane. The exhausted chips are also passed through the mill and the expressed juice, tested. The per cent. of sucrose in exhausted chips subtracted from the per cent. sucrose in the fresh chips, divided by the latter per cent. and multiplied by 100, gives per cent. ratio of sucrose extracted to the total sucrose present.

Samples of juices and chips should be analyzed as expeditiously as possible after the sample is drawn, as, on standing, changes frequently take place which affect the value of the analytical results.

*Determination of Fiber.*—Twenty grams of fresh chips are weighed out and placed in a beaker or Erlenmeyer flask. The samples then washed repeatedly with water of a temperature of from 85° to 90° C., the washings each time being poured off. A temperature of the boiling point must be avoided in the early part of the operation, as coagulation of albuminoids will ensue and the extraction of soluble matters will thereby be hindered. The washing by decantation is continued until soluble albuminoids are dissolved out, when the contents of the flask are boiled with water several times, being treated with fresh portions after each decantation. The insoluble residue is now brought upon a weighed and dried muslin or asbestos filter, and the washing with boiling water is continued upon the filter. The filter and contents are then dried in air bath at 100 to 110° C., and weighed: the increase in weight is amount of fiber. Per cent. of fiber deducted from 100, gives per cent. of juice.

#### REPORT OF COMMITTEE ON METHODS OF CHEMICAL ANALYSIS.

With a view to the improvement of the present methods of sugar analysis and the elimination of errors in the processes now used in the determination of the constituents of cane juices, syrups, molasses, etc., the committee on methods of chemical analysis, of the Sugar Chemists' Association, during the past summer, made a series of investigations leading to the results herein given.

These investigations were confined almost exclusively to polariscopic methods, especially as regards the determination of sucrose in the presence of invert sugars. As the necessity of double polarization in the analysis of molasses, syrups and immature sorghum and cane juices is almost universally recognized by chemists conversant with the subject, it was deemed advisable

to first make some experiments with reference to the correct expression of the formula used in connection with Clerget's method of inversion. The inaccuracy of results obtained by the use of Clerget's original constant of 144 having become apparent in a number of instances, experiments were made to test the correctness of Landolt's revised figure of 142.4. Though it was comparatively easy, with the aid of a freezing mixture, to reduce the temperature of the invert solution used to 0 deg. C., yet there was such a condensation of moisture on the glasses of the polariscope tubes, that it was impossible to make any satisfactory readings of the instrument. The difficulty, too, of maintaining the low temperature of 0 deg. C., with an external atmospheric temperature much higher, suggested the necessity of conducting the experiments in an atmosphere approximating in temperature, as nearly as possible, that of the solution under examination.

Accordingly, through the courtesy of the New Orleans Cold Storage Company, the committee was permitted to make its investigations in one of their storage rooms, where a constant temperature of about 31 degrees Fahr. was maintained. The sugar used in the experiments was cane sugar, crystallized in unusually perfect rhombic prisms, a normal weight of which, when dissolved in water and made up to a bulk of 100 cubic centimeters, at 17.5° C., gave a reading at 17.5° C., of 100, as determined by three independent observers. The normal sucrose solution when reduced to a temperature of 4 deg. C., however, showed a reading of only 99.7. Fifty cc. of this solution were next inverted in the manner prescribed by Clerget, hydrochloric acid to the amount of one-tenth of the volume of the solution being added.

The temperature of the solution having been lowered to about -2 deg. C., it was placed in a polariscope tube provided with a centre tubulure for the insertion of a thermometer; at -1 deg. C. a reading to the left of 42.9 was obtained, which, when corrected for temperature gave 42.4. At  $-3/4^{\circ}$  C. the solution read 42.46, corrected for temperature, 42.34; at 0 deg. C. the reading was 42.35; at  $+3/4^{\circ}$  C. the reading was 42.02; corrected for temperature, 42.39.

The solution was next raised by a gentle heat to about 15° C., replaced in the tube, and several additional readings were made, but the temperature fell so rapidly that no satisfactory duplicate results could be obtained. In these experiments, accurately calibrated flasks and tubes were employed, the gaugings were made at 17.5° C., and polariscopic readings were made in duplicate, and in some instances by three observers. It was quite noticeable, too, that at the low temperature employed, the solution could be read with a clearness and precision unattainable, even at the ordinary temperature of the air. These results would appear to confirm very fully the correctness of the constant 142.4, as obtained by Landolt.

In order to test the effect of the presence of invert sugar, even in comparatively small quantities, upon the direct readings of the polariscope, it was determined to mix varying proportions of the chemically pure invert sugar solution with a given volume of a pure sucrose solution, and to test



the solutions thus obtained by both single and double polarization. Samples from the same lot of chemically pure cane sugar were furnished each member of the committee, and the subsequent experiments were performed independently in three different laboratories. A normal sucrose solution, prepared by dissolving 26.048 grammes of sugar in water and diluting to a bulk of 100 cc., was first made up and designated as solution A. A similar solution was inverted as previously described, and gave the following readings, as determined by the respective members of the committee :

Martin.	Bird Deg. C.	Ross. Deg. C.
	26 at 33.3	27.4 at 30.5
	26. + 16.65	27.40 + 15.25
Corrected for temperature . . 42.5	42.65	42.65

These results, as corrected for temperature, seem to indicate that the usual compensation of one-half of a degree of the saccharimeter scale for each degree of temperature is a little high, though near enough for all practical purposes. A standard invert solution, neutralized with sodium carbonate and made up to 110 cc., was designated as solution B. Portions of the solutions were then mixed in the following proportions :

- 10 cc. of solution A and 1 cc. solution B were made up to 100 cc., forming solution 1.
- 10 cc. of solution A and 2 cc. solution B were made up to 100 cc., forming solution 2.
- 10 cc. of solution A and 3 cc. solution B were made up to 100 cc., forming solution 3.
- 10 cc. of solution A and 4 cc. solution B were made up to 100 cc., forming solution 4.
- 10 cc. of solution A and 5 cc. solution B were made up to 100 cc., forming solution 5.
- 10 cc. of solution A and 6 cc. solution B were made up to 100 cc., forming solution 6.
- 10 cc. of solution A and 7 cc. solution B were made up to 100 cc., forming solution 7.
- 10 cc. of solution A and 8 cc. solution B were made up to 100 cc., forming solution 8.
- 10 cc. of solution A and 9 cc. solution B were made up to 100 cc., forming solution 9.
- 10 cc. of solution A and 10 cc. solution B were made up to 100 cc., forming solution 10.

The solutions thus obtained were subjected to polariscopic tests, the direct readings in two of the laboratories being made in 400 millimeter tubes, with a double compensating Schmidt and Haensch instrument.

The temperatures of the solutions at the time of reading were carefully noted and are given below :

## RESULTS OF SINGLE POLARIZATION TESTS.

	Martin.	Bird.	Ross.
	Deg. C.	Deg. C.	Deg. C.
Solution 1 . . . . .	9.80 at 30	9.8 at 33	9.75 at 29.5
Solution 2 . . . . .	9.60 at 29.5	9.5 at 33	9.55 at 30
Solution 3 . . . . .	9.30 at 29.5	9.3 at 33	9.35 at 30.5
Solution 4 . . . . .	9.20 at 30	9.1 at 33	9.10 at 30
Solution 5 . . . . .	8.80 at 29.5	8.9 at 33	8.85 at 29
Solution 6 . . . . .	8.60 at 29.5	8.7 at 33	8.60 at 29.5
Solution 7 . . . . .	8.40 at 30	8.5 at 33	8.35 at 29.5
Solution 8 . . . . .	8.20 at 30	8.2 at 33	8.10 at 29.5
Solution 9 . . . . .	7.90 at 30	8. at 33	7.85 at 29
Solution 10 . . . . .	7.60 at 30	7.7 at 33	7.60 at 29.5
Average temperature .	29.80	33	29.6

From the above results it will be seen that for each cubic centimeter of the invert solution B, mixed with 10 cc. of the sucrose solution A, there has been an average decrease in the apparent per cent. of sucrose of 0.24 at an average temperature of 29.8° C., 0.23 at a temperature of 33° C., and 0.24 at 29.6 C. (The quantity of invert sugar in one cubic centimetre of solution B, when diluted to 100 cc., gives an equivalent of .957 per cent. of invert sugar.) The normal sucrose solution, when inverted and made up to 100 cc. gives a reading in a 200 millimeter tube of 38.5, at 0° C. ( $\frac{42.4}{1.1} = 38.5 +$ ); at 29.8° C., the reading would be  $\frac{42.4 - \frac{1}{2}(29.8)}{1.1} = 25$ ; at 33° C. the reading would be  $\frac{42.4 - \frac{1}{2}(33)}{1.1} = 23.55$ ; at 29.6° the reading would be  $\frac{42.4 - \frac{1}{2}(29.6)}{1.1} = 25.1$ .

Accordingly one cc. of such a solution, diluted to 100 cc. should give a reading to the left at 29.8° C. of .25; at 33° C. a reading of .2355; at 29.6° of .251; whereas, the experiments indicate that the right handed readings show deviations to the left of 0.24, 0.23 and 0.24, respectively, for each cc. of the invert solution present—a comparatively close approximation of the practical to the theoretical results. In two of the laboratories double polarization tests of the same solutions were made with the following results:

Constant used . . . . .	Bird.	Ross.	
	142.4	142.4	144
	Per cent. sucrose.	Per cent.	Per cent.
1 . . . . .	10.07	10.07	9.95
2 . . . . .	9.91	10.08	9.96
3 . . . . .	9.95	10.08	9.96
4 . . . . .	9.96	10.05	9.92
5 . . . . .	9.99	10.08	9.96
6 . . . . .	10.03	10.05	9.92
7 . . . . .	10.01	10.03	9.90
8 . . . . .	10.04	10.01	9.88
9 . . . . .	10.08	9.99	9.87
10 . . . . .	10.12	10.05	9.92

The results given in the first and second columns are obtained by the use of the formula  $R = \frac{100 s}{142.4 - \frac{1}{2} T.}$  while the figures in the third column are obtained from the old formula,  $R = \frac{100 s}{144 - \frac{1}{2} T.}$  The average variations from the theoretical percentage with the use of the constant 142.4 were .054 and .051, while with the figure 144 the variation was .076 per cent. Had 400 mm. tubes been employed for invert solutions, as well as in single polarization tests, the discrepancies would have, without doubt, been much smaller.

In addition to the polariscope determinations given above, the actual amounts, by weight, of invert sugar in the solution examined were determined by means of Fehling's solution. The following are the results obtained, together with the theoretical amounts of invert sugar contained in the solutions :

Theoretical Amounts.		Amounts Obtained by Use of Fehling's Solution.	
	Gram.	Bird. Gram.	Ross. Gram.
Solution 1 . . . . .	.2792	.253	.2531
" 2 . . . . .	.4984	.506	.5074
" 3 . . . . .	.7476	.7438	.7445
" 4 . . . . .	.9968	.9918	.9950
" 5 . . . . .	1.246	1.2346	1.244
" 6 . . . . .	1.4952	1.5031	1.4854
" 7 . . . . .	1.7444	1.7659	1.733
" 8 . . . . .	1.9936	2.004	1.952
" 9 . . . . .	2.2423	2.2673	2.227
" 10 . . . . .	2.492	2.530	2.4697

The alkaline cupric liquor, used in the above determination, was Violette's modification of Fehling's solution, and was standardized by means of a solution of C. P. anhydrous glucose. It will be seen by reference to the above table that approximately one-fourth gram, or multiple thereof of invert sugar, was present in each of the solutions examined, and that for each one-fourth gram present in 100 cc. of the solution there was an average laevo-rotary effect of 0.24, 0.23 and 0.24, at the temperatures of 29.8°, 33° and 29.6°. At lower temperature it is readily apparent that this influence would be much greater. The results of these experiments, therefore, would seem to indicate the necessity of making due compensation in sucrose determinations for the presence of invert sugar even in small proportions.

The committee would, in view of the results of the experiments in double polarization, recommend the use of the constant 142.4 in all such determinations hereafter. The committee acknowledge their indebtedness to Mr. Colcock, the Secretary of the Sugar Exchange, for courtesies extended ; to Mr. James Thibaut, who kindly placed his laboratory and apparatus at our disposal ; to Mr. Bridges, the Secretary, Mr. Walker, and other officials of the

New Orleans Cold Storage Company, for numerous favors shown during the progress of the experiments.

Respectfully,

B. B. ROSS, *Chairman.*

MAURICE BIRD,

W. P. MARTIN,

*Committee on Methods of Chemical Analysis.*

NOTE.—In determinations of sucrose by inversion, where accuracy is desired, instead of the regular titration, the amount of copper sub-oxide should be determined gravimetrically according to one of the methods of Tucker.

The following table, calculated with the use of the formula  $R = \frac{142.4 - \frac{1}{2} T.}{100 S}$ , is published, it is believed, in this form for the first time, and it will be found to materially shorten the labor of calculation of double polarization results.

*Method of Using the Table.*—The columns on the extreme left and right of the table contain sums of direct and invert readings. The other columns are headed with the number of degrees Centigrade of temperature, ranging from 10° to 35°, at which any reading may be made, and contain per cents. sucrose corresponding to the sums given in the left and right hand columns. Suppose a solution is found to give a right and left handed reading whose sum is 45.3, the invert solution being read at 25° C. Look in the column headed 25°, opposite 40.0, and we find the number 30.79; now look in the same column opposite 5.3, and the number 4.8, which is there found, is added to 30.79, giving 34.87 as the per cent. of sucrose corresponding to the sum 45.3 at 25° C.

# CLERGEY'S DOUBLE POLARIZATION TABLE, REVISED.

CALCULATED WITH THE USE OF THE CONSTANT 142.4.

Per Cents of Sucrose Corresponding to Sums of Direct and Invert Readings, at Given Degrees Temperature, Centigrade (10°-35°).																										Sums	
10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	Sums	
1	07	07	07	07	07	07	07	07	08	08	08	08	08	08	08	08	08	08	08	08	08	08	08	08	08	1	
2	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	16	16	16	16	16	16	16	16	2	
3	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	3	
4	29	29	29	29	29	29	29	29	29	29	29	29	29	29	29	29	29	29	29	29	29	29	29	29	29	4	
5	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36	5	
6	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44	44	6	
7	51	51	51	51	51	51	51	51	51	51	51	51	51	51	51	51	51	51	51	51	51	51	51	51	51	7	
8	58	58	58	58	58	58	58	58	58	58	58	58	58	58	58	58	58	58	58	58	58	58	58	58	58	8	
9	65	65	65	65	65	65	65	65	65	65	65	65	65	65	65	65	65	65	65	65	65	65	65	65	65	9	
10	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	72	10	
11	79	79	79	79	79	79	79	79	79	79	79	79	79	79	79	79	79	79	79	79	79	79	79	79	79	11	
12	86	86	86	86	86	86	86	86	86	86	86	86	86	86	86	86	86	86	86	86	86	86	86	86	86	12	
13	87	88	88	88	88	88	88	88	88	88	88	88	88	88	88	88	88	88	88	88	88	88	88	88	88	13	
14	102	102	102	103	103	104	104	105	105	105	106	107	107	107	107	108	108	109	109	109	109	109	109	109	109	14	
15	109	110	110	110	110	110	110	110	110	110	110	110	110	110	110	110	110	110	110	110	110	110	110	110	110	15	
16	116	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	16	
17	124	124	124	124	124	124	124	124	124	124	124	124	124	124	124	124	124	124	124	124	124	124	124	124	124	17	
18	131	131	131	131	131	131	131	131	131	131	131	131	131	131	131	131	131	131	131	131	131	131	131	131	131	18	
19	138	139	139	139	139	139	139	139	139	139	139	139	139	139	139	139	139	139	139	139	139	139	139	139	139	19	
20	146	146	146	146	146	146	146	146	146	146	146	146	146	146	146	146	146	146	146	146	146	146	146	146	146	20	
21	153	153	153	153	153	153	153	153	153	153	153	153	153	153	153	153	153	153	153	153	153	153	153	153	153	21	
22	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	160	22	
23	167	168	168	168	168	168	168	168	168	168	168	168	168	168	168	168	168	168	168	168	168	168	168	168	168	23	
24	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	175	24	
25	182	183	183	183	183	183	183	183	183	183	183	183	183	183	183	183	183	183	183	183	183	183	183	183	183	25	
26	189	190	190	190	190	190	190	190	190	190	190	190	190	190	190	190	190	190	190	190	190	190	190	190	190	26	
27	196	197	198	198	198	198	198	198	198	198	198	198	198	198	198	198	198	198	198	198	198	198	198	198	198	27	
28	204	204	205	205	205	205	205	205	205	205	205	205	205	205	205	205	205	205	205	205	205	205	205	205	205	28	
29	211	212	212	213	213	213	213	213	213	213	213	213	213	213	213	213	213	213	213	213	213	213	213	213	213	29	
30	218	219	220	220	220	220	220	220	220	220	220	220	220	220	220	220	220	220	220	220	220	220	220	220	220	30	
31	226	226	227	227	227	227	227	227	227	227	227	227	227	227	227	227	227	227	227	227	227	227	227	227	227	31	
32	233	234	235	235	235	235	235	235	235	235	235	235	235	235	235	235	235	235	235	235	235	235	235	235	235	32	
33	241	241	242	243	243	243	243	243	243	243	243	243	243	243	243	243	243	243	243	243	243	243	243	243	243	33	
34	248	249	250	250	250	250	250	250	250	250	250	250	250	250	250	250	250	250	250	250	250	250	250	250	250	34	
35	255	256	257	257	257	257	257	257	257	257	257	257	257	257	257	257	257	257	257	257	257	257	257	257	257	35	
36	262	263	264	264	264	264	264	264	264	264	264	264	264	264	264	264	264	264	264	264	264	264	264	264	264	36	
37	269	270	271	271	271	271	271	271	271	271	271	271	271	271	271	271	271	271	271	271	271	271	271	271	271	37	
38	276	277	278	278	278	278	278	278	278	278	278	278	278	278	278	278	278	278	278	278	278	278	278	278	278	38	
39	284	285	286	286	286	286	286	286	286	286	286	286	286	286	286	286	286	286	286	286	286	286	286	286	286	39	
40	291	292	293	293	293	293	293	293	293	293	293	293	293	293	293	293	293	293	293	293	293	293	293	293	293	40	
41	298	299	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	300	41	
42	306	307	308	308	308	308	308	308	308	308	308	308	308	308	308	308	308	308	308	308	308	308	308	308	308	42	
43	313	314	315	315	315	315	315	315	315	315	315	315	315	315	315	315	315	315	315	315	315	315	315	315	315	43	
44	320	321	322	322	322	322	322	322	322	322	322	322	322	322	322	322	322	322	322	322	322	322	322	322	322	44	
45	327	328	329	329	329	329	329	329	329	329	329	329	329	329	329	329	329	329	329	329	329	329	329	329	329	45	
46	335	336	337	337	337	337	337	337	337	337	337	337	337	337	337	337	337	337	337	337	337	337	337	337	337	46	
47	343	344	345	345	345	345	345	345	345	345	345	345	345	345	345	345	345	345	345	345	345	345	345	345	345	47	
48	349	351	352	352	352	352	352	352	352	352	352	352	352	352	352	352	352	352	352	352	352	352	352	352	352	48	
49	357	358	359	359	359	359	359	359	359	359	359	359	359	359	359	359	359	359	359	359	359	359	359	359	359	49	

5.6	4.97	4.99	4.11	4.12	4.14	4.15	4.17	4.18	4.20	4.21	4.23	4.25	4.26	4.29	4.31	4.32	4.34	4.35	4.37	4.39	4.40	4.42	4.44	4.46	4.47	4.49	4.51	4.53	4.55	4.56	5.7	
5.7	4.15	4.16	4.18	4.19	4.21	4.23	4.24	4.26	4.27	4.29	4.31	4.32	4.34	4.35	4.37	4.39	4.40	4.42	4.43	4.45	4.46	4.48	4.50	4.52	4.53	4.55	4.57	4.59	4.61	4.63	4.64	5.8
5.8	4.22	4.24	4.25	4.27	4.28	4.30	4.32	4.33	4.35	4.36	4.38	4.40	4.42	4.43	4.45	4.46	4.48	4.49	4.51	4.52	4.54	4.56	4.58	4.60	4.61	4.63	4.65	4.67	4.69	4.70	4.72	5.9
5.9	4.29	4.31	4.33	4.34	4.36	4.37	4.39	4.41	4.42	4.44	4.46	4.47	4.49	4.51	4.52	4.54	4.55	4.57	4.58	4.60	4.62	4.64	4.65	4.67	4.69	4.71	4.73	4.75	4.77	4.78	4.80	6.0
6.0	4.37	4.38	4.40	4.41	4.43	4.45	4.46	4.48	4.50	4.51	4.53	4.55	4.57	4.58	4.60	4.62	4.64	4.66	4.68	4.70	4.71	4.73	4.75	4.77	4.79	4.81	4.83	4.85	4.86	4.88	6.1	
6.1	4.44	4.46	4.47	4.49	4.51	4.52	4.54	4.56	4.57	4.59	4.61	4.62	4.64	4.66	4.68	4.70	4.72	4.74	4.75	4.77	4.79	4.81	4.83	4.85	4.87	4.89	4.91	4.92	4.94	4.96	6.2	
6.2	4.51	4.53	4.55	4.56	4.58	4.60	4.61	4.63	4.64	4.67	4.68	4.70	4.72	4.74	4.75	4.77	4.79	4.81	4.83	4.85	4.87	4.89	4.91	4.93	4.95	4.96	4.98	5.00	5.02	5.04	6.3	
6.3	4.59	4.60	4.62	4.63	4.65	4.67	4.69	4.70	4.72	4.74	4.76	4.78	4.79	4.81	4.83	4.85	4.87	4.89	4.91	4.93	4.95	4.97	4.98	5.00	5.02	5.04	5.06	5.08	5.10	5.12	6.4	
6.4	4.66	4.67	4.69	4.71	4.73	4.74	4.76	4.78	4.80	4.82	4.83	4.85	4.87	4.89	4.91	4.93	4.95	4.97	4.98	5.00	5.02	5.04	5.06	5.08	5.10	5.12	5.14	5.16	5.18	5.20	6.5	
6.5	4.73	4.75	4.77	4.78	4.80	4.82	4.84	4.85	4.87	4.89	4.91	4.93	4.95	4.97	4.98	5.00	5.02	5.04	5.06	5.08	5.10	5.12	5.14	5.16	5.18	5.20	5.22	5.24	5.26	5.28	6.6	
6.6	4.80	4.82	4.84	4.86	4.87	4.89	4.91	4.93	4.95	4.97	4.99	5.00	5.02	5.04	5.06	5.08	5.10	5.12	5.14	5.16	5.18	5.20	5.22	5.24	5.26	5.28	5.30	5.32	5.34	5.36	6.7	
6.7	4.88	4.89	4.91	4.93	4.95	4.97	4.99	5.00	5.02	5.04	5.06	5.08	5.10	5.12	5.14	5.16	5.18	5.20	5.22	5.24	5.26	5.28	5.30	5.32	5.34	5.36	5.38	5.40	5.42	5.44	6.8	
6.8	4.95	4.97	4.99	5.00	5.02	5.04	5.06	5.08	5.10	5.12	5.14	5.16	5.18	5.20	5.22	5.24	5.26	5.28	5.30	5.32	5.34	5.36	5.38	5.40	5.42	5.44	5.46	5.48	5.50	5.52	6.9	
6.9	5.02	5.04	5.06	5.08	5.10	5.12	5.14	5.16	5.18	5.20	5.22	5.24	5.26	5.28	5.30	5.32	5.34	5.36	5.38	5.40	5.42	5.44	5.46	5.48	5.50	5.52	5.54	5.56	5.58	5.60	7.0	
7.0	5.09	5.11	5.13	5.15	5.17	5.19	5.21	5.23	5.25	5.27	5.29	5.31	5.33	5.35	5.37	5.39	5.41	5.43	5.45	5.47	5.49	5.51	5.53	5.55	5.57	5.59	5.61	5.63	5.65	5.67	7.1	
7.1	5.17	5.19	5.21	5.22	5.24	5.26	5.28	5.30	5.32	5.34	5.36	5.38	5.40	5.42	5.44	5.46	5.48	5.50	5.52	5.54	5.56	5.58	5.60	5.62	5.64	5.66	5.68	5.70	5.72	7.2		
7.2	5.24	5.26	5.28	5.30	5.32	5.34	5.36	5.38	5.40	5.42	5.44	5.46	5.48	5.50	5.52	5.54	5.56	5.58	5.60	5.62	5.64	5.66	5.68	5.70	5.72	5.74	5.76	5.78	5.80	7.3		
7.3	5.31	5.33	5.35	5.37	5.39	5.41	5.43	5.45	5.47	5.49	5.51	5.53	5.55	5.57	5.59	5.61	5.63	5.65	5.67	5.69	5.71	5.73	5.75	5.77	5.79	5.81	5.83	5.85	5.87	7.4		
7.4	5.39	5.41	5.43	5.44	5.46	5.48	5.50	5.52	5.54	5.56	5.58	5.60	5.62	5.64	5.66	5.68	5.70	5.72	5.74	5.76	5.78	5.80	5.82	5.84	5.86	5.88	5.90	5.92	5.94	7.5		
7.5	5.46	5.48	5.50	5.52	5.54	5.56	5.58	5.60	5.62	5.64	5.66	5.68	5.70	5.72	5.74	5.76	5.78	5.80	5.82	5.84	5.86	5.88	5.90	5.92	5.94	5.96	5.98	6.00	6.02	6.04	7.6	
7.6	5.53	5.55	5.57	5.59	5.61	5.63	5.65	5.67	5.69	5.71	5.73	5.75	5.77	5.79	5.81	5.83	5.85	5.87	5.89	5.91	5.93	5.95	5.97	5.99	6.01	6.03	6.05	6.07	6.09	6.11	7.7	
7.7	5.60	5.62	5.65	5.67	5.69	5.71	5.73	5.75	5.77	5.79	5.81	5.83	5.85	5.87	5.89	5.91	5.93	5.95	5.97	5.99	6.01	6.03	6.05	6.07	6.09	6.11	6.13	6.15	6.17	6.19	7.8	
7.8	5.68	5.70	5.72	5.74	5.76	5.78	5.80	5.82	5.84	5.86	5.88	5.90	5.92	5.94	5.96	5.98	6.00	6.02	6.04	6.06	6.08	6.10	6.12	6.14	6.16	6.18	6.20	6.22	6.24	7.9		
7.9	5.75	5.77	5.79	5.81	5.83	5.85	5.87	5.89	5.91	5.93	5.95	5.97	5.99	6.01	6.03	6.05	6.07	6.09	6.11	6.13	6.15	6.17	6.19	6.21	6.23	6.25	6.27	6.29	6.31	6.33	8.0	
8.0	5.82	5.84	5.87	5.89	5.91	5.93	5.95	5.97	5.99	6.01	6.03	6.05	6.07	6.09	6.11	6.13	6.15	6.17	6.19	6.21	6.23	6.25	6.27	6.29	6.31	6.33	6.35	6.37	6.39	6.41	8.1	
8.1	5.90	5.92	5.94	5.96	5.98	6.00	6.02	6.04	6.06	6.08	6.10	6.12	6.14	6.16	6.18	6.20	6.22	6.24	6.26	6.28	6.30	6.32	6.34	6.36	6.38	6.40	6.42	6.44	6.46	6.48	8.2	
8.2	5.97	5.99	6.01	6.03	6.05	6.07	6.09	6.11	6.13	6.15	6.17	6.19	6.21	6.23	6.25	6.27	6.29	6.31	6.33	6.35	6.37	6.39	6.41	6.43	6.45	6.47	6.49	6.51	6.53	6.55	8.3	
8.3	6.04	6.06	6.09	6.11	6.13	6.15	6.17	6.19	6.21	6.23	6.25	6.27	6.29	6.31	6.33	6.35	6.37	6.39	6.41	6.43	6.45	6.47	6.49	6.51	6.53	6.55	6.57	6.59	6.61	6.63	8.4	
8.4	6.11	6.14	6.16	6.18	6.20	6.22	6.24	6.26	6.28	6.30	6.32	6.34	6.36	6.38	6.40	6.42	6.44	6.46	6.48	6.50	6.52	6.54	6.56	6.58	6.60	6.62	6.64	6.66	6.68	6.70	8.5	
8.5	6.19	6.21	6.23	6.25	6.27	6.29	6.31	6.33	6.35	6.37	6.39	6.41	6.43	6.45	6.47	6.49	6.51	6.53	6.55	6.57	6.59	6.61	6.63	6.65	6.67	6.69	6.71	6.73	6.75	6.77	8.6	
8.6	6.26	6.28	6.30	6.32	6.34	6.36	6.38	6.40	6.42	6.44	6.46	6.48	6.50	6.52	6.54	6.56	6.58	6.60	6.62	6.64	6.66	6.68	6.70	6.72	6.74	6.76	6.78	6.80	6.82	6.84	8.7	
8.7	6.33	6.35	6.38	6.40	6.42	6.44	6.46	6.48	6.50	6.52	6.54	6.56	6.58	6.60	6.62	6.64	6.66	6.68	6.70	6.72	6.74	6.76	6.78	6.80	6.82	6.84	6.86	6.88	6.90	6.92	8.8	
8.8	6.40	6.43	6.45	6.48	6.50	6.52	6.55	6.57	6.60	6.62	6.65	6.67	6.70	6.72	6.75	6.77	6.80	6.82	6.85	6.87	6.90	6.93	6.96	6.99	7.01	7.04	7.07	7.10	7.13	8.9		
8.9	6.48	6.50	6.52	6.55	6.57	6.60	6.62	6.65	6.67	6.70	6.72	6.75	6.77	6.80	6.82	6.85	6.87	6.90	6.93	6.96	6.99	7.01	7.04	7.07	7.10	7.13	7.16	7.19	7.22	9.0		
9.0	6.55	6.58	6.60	6.62	6.65	6.67	6.70	6.72	6.75	6.77	6.80	6.82	6.85	6.87	6.90	6.93	6.96	6.99	7.01	7.04	7.07	7.10	7.13	7.16	7.19	7.22	7.25	7.28	7.31	9.1		
9.1	6.63	6.65	6.67	6.70	6.72	6.75	6.77	6.80	6.82	6.85	6.87	6.90	6.93	6.96	6.99	7.01	7.04	7.07	7.10	7.13	7.16	7.19	7.22	7.25	7.28	7.31	7.34	7.37	7.40	9.2		
9.2	6.70	6.72	6.74	6.77	6.79	6.82	6.85	6.87	6.90	6.92	6.95	6.97	7.00	7.03	7.05	7.08	7.10	7.13	7.16	7.19	7.22	7.25	7.28	7.31	7.34	7.37	7.40	7.43	7.46	9.3		
9.3	6.77	6.79	6.82	6.84	6.87	6.89	6.92	6.95	6.97	6.99	7.02	7.04	7.07	7.10	7.13	7.15	7.18	7.20	7.23	7.26	7.29	7.32	7.35	7.38	7.41	7.44	7.47	7.50	7.53	9.4		
9.4	6.84	6.87	6.89	6.92	6.94	6.97	6.99	7.02	7.04	7.07	7.09	7.12	7.14	7.17	7.19	7.22	7.25	7.28	7.31	7.34	7.37	7.40	7.43	7.46	7.49	7.52	7.55	7.58	7.61	9.5		
9.5	6.90	6.94	6.96	6.99	7.02	7.04	7.07	7.09	7.12	7.14	7.17	7.20	7.23	7.26	7.29	7.32	7.35	7.38	7.41	7.44	7.47	7.50	7.53	7.56	7.59	7.62	7.65	7.68	7.71	9.6		
9.6	6.99	7.03	7.06	7.09	7.12	7.14	7.17	7.20	7.23	7.26	7.29	7.32	7.35	7.38	7.41	7.44	7.47	7.50	7.53	7.56	7.59	7.62	7.65	7.68	7.71	7.74	7.77	7.80	7.83	9.7		
9.7	7.06	7.10	7.11	7.14	7.16	7.19	7.22	7.24	7.27	7.30	7.33	7.36	7.39	7.42	7.45	7.48	7.51	7.54	7.57	7.60	7.63	7.66	7.69	7.72	7.75	7.78	7.81	7.84	7.87	9.8		
9.8	7.13	7.16	7.18	7.21	7.24	7.26	7.29	7.32	7.35	7.37	7.40	7.43	7.46	7.49	7.52	7.55	7.58	7.61	7.64	7.67	7.70	7.73	7.76	7.79	7.82	7.8						

## GADOLINITE FROM LLANO COUNTY, TEXAS.

By E. GOLDSMITH.

The specimen so called which came from the above locality is in the Wm. M. Vaux Collection of the Phila. Academy of Natural Sciences, and is of unusual size. It appears as a rough orthorhombic crystal. A piece broken off at one end revealed the fact that the crystal was not homogeneous throughout. Within, a glassy material surrounded by a rather thick layer of perfectly dull appearance indicated that it was made up of at least two different minerals. I procured from the mineral dealer fragments of these two substances for investigation. The inner or vitreous substance proved to be Gadolinite. In mass the color is deep black and opaque, but when a thin plate is prepared by grinding, it appears green. Beneath the microscope, apparently, all is homogeneous; only a few black minute spots are noticed. Between the two nicol prisms it was not at all affected, even when the ray passed through it parallel or convergent. The field of the crossed nicols became darker when the plate was placed between them. The apparent form is therefore misleading. Supposing the optical laws of crystallized bodies to be correct, I arrive at the conclusion that the crystal found is either isometric or pseudomorphous.

Fracture conchoidal and uneven. Hardness = 6. Sp. gr. = 4.276. It affords no streak on unglazed porcelain, and it is brittle; the powder is grayish-green.

For analysis, the substance was selected with care, and was easily decomposed by hydrochloric acid, the silica gelatinizing.

The result was as follows:

Silica . . . . .	25.70	per cent.	O = 13.7
Yttria . . . . .	58.30	"	" = 12
Iron Monoxide . . . . .	15.52	"	" = 3.44
Glucina . . . . .	2.10	"	" = 1.32

The oxygen ratios of the silica to the monoxys is as 1 : 1.2, therefore nearly 1 : 1 which corresponds fairly with one of Berlin's analysis of material from Ytterby, except that he found in all his investigations cerium, small quantities of alkalis, and alkaline earths. I took special pains to trace the presence of cerium, but could not detect it. The yttria found was dissolved as nitrate, and

the concentrated solution examined spectroscopically for erbia, but none was found. I confess to not knowing a reliable process for separating either erbia or terbia, hence the results obtained can only be considered approximate.

The material enveloping the Gadolinite seems to be amorphous; dull, with an uneven fracture and brittle; its color is grayish brown; streak red—when powdered, bright red.

It was found necessary to float off the suspended part in water from another portion which was not decomposable by hydrochloric acid, and this repeated until a sample was wholly decomposable by that acid. The silica did not gelatinize.

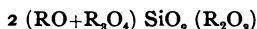
Hardness = 3. Sp. Gr. = 3.494.

Not fusible before the blowpipe. The fluxes indicated iron; heated in a tube it gave water. Heated with carb. soda upon charcoal it afforded a dark-brown slag.

The analysis indicated great complexity of mixture.

SiO <sub>2</sub>	18.145	per cent.	O = 9.676
Ce <sub>2</sub> O <sub>3</sub>	20.662	"	O = 16.773
Fe <sub>2</sub> O <sub>3</sub>	26.026	"	O = 7.807
YO	21.854	"	O = 4.500
CaO	3.642	"	O = 1.040
MgO	0.214	"	O = 0.085
HO	9.761	"	O = 8.676

The approximate O ratios of the sum of the monoxys are equal to the tetroxys, or about two, whilst the O ratio of the dioxys and the sesquioxys are each nearly one, hence this general expression is proposed:—



The question whether this substance is a mixture or not, I endeavored to solve by this consideration: sesquioxides of iron as goëthite, limonite, etc., are respectively soluble to some extent in a strong solution of citric acid; if any of these oxys should be mixed or occur as such in the mineral a test with that acid would indicate the fact. The test was made; for several hours the fine red mineral powder was kept in contact with a strong solution of citric acid at the ordinary temperature, about 70° F. and agitated occasionally with no effect. If heated on steam bath the effect was very slight. It seems, therefore, that the substance is not a mix-



ture, but a hydrated tribasic silicate in which the water is substituted for any other monoxyd.

The yttria was also tested optically for erbia with negative result.

I am not aware that this material over the Gadolinite has been named. I propose for it the name METAGADOLINITE.

### THE COMPOSITION OF BOILER SCALE.

BY THOS. B. STILLMAN.

The results of an analysis of boiler scale usually represent the lime and magnesia as carbonates with a portion of the former as sulphate—on the general principle that the scale made continues to exist in the form in which it was precipitated. In those portions of the boiler where the direct heat does not come in contact with it, the scale remains unchanged after formation, but the conditions are altered where the scale is subjected to intense heat. In the latter case, while the deposition of the scale-forming material at first occurs as carbonate and sulphate, the gradual heating expels some of the carbonic acid, and the oxides of calcium and magnesium are formed.

That portion of the scale nearest the iron and to the heat loses more of its carbonic acid, and becomes caustic so long as the fire continues.

As soon, however, as the fires are drawn, the oxides of calcium and magnesium become hydrated by absorption of water.

If now a sample of the scale were taken for analysis, the water of hydration becomes an important factor in the analysis :

A sample of scale from some boilers at Birmingham, Ala., recently submitted to me for analysis, gave the following result :

Silica and Clay . . . . .	11.70%
Fe <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> . . . . .	2.81
CaO . . . . .	11.62
MgO . . . . .	41.32
CO <sub>2</sub> . . . . .	6.92
SO <sub>3</sub> . . . . .	0.96
H <sub>2</sub> O (of hydration) . . . . .	21.78
H <sub>2</sub> O (moisture at 212° F.) . . . . .	0.69
Undetermined . . . . .	0.20
Total, 100.00%	

An examination of this analysis shows an unusually small amount of carbonic and sulphuric acids, a large amount of water and of magnesia.

The great excess of the latter over the lime indicates that the water from which the scale was formed is a magnesia water, but its presence in this amount does not in any way alter the conditions of the problem.

With less than one per cent. of sulphuric acid and less than seven per cent. of carbonic acid, the oxides of calcium and magnesium could not exist in their entirety as carbonates or sulphates, for, combining the above acids to form carbonates and sulphates the result indicated over twenty per cent. lacking in the 100 parts.

The determinations of the carbonic and sulphuric acids were in duplicate and in every way satisfactory, while no organic matter of any amount was indicated in the analysis.

The large percentage of the oxides of calcium and magnesium left after combination with the acids suggested water of hydration.

A sample of the scale (dried at 100° C.) was transferred to a platinum crucible and heated over the blast lamp to a constant weight. The loss of weight was over 28 per cent., and, of course, included the carbonic, but not the sulphuric acid.

To check this result, a sample of the dried scale was ignited in a combustion tube and the H<sub>2</sub>O collected in a weighed chloride of calcium tube. The result was 21.78% of water of hydration.

This satisfied the conditions existing, and the combinations gave as follows :

Silica and Clay . . . . .	11.70%
Fe <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> . . . . .	2.81
CaSO <sub>4</sub> . . . . .	1.69
CaCO <sub>3</sub> . . . . .	5.45
MgCO <sub>3</sub> . . . . .	7.36
Ca(OH) <sub>2</sub> . . . . .	13.70
Mg(OH) <sub>2</sub> . . . . .	56.37
H <sub>2</sub> O (moisture at 212° F.) . . . . .	0.69
Undetermined . . . . .	0.20
<hr/>	
Total, 99.97%	

A section of the scale was subjected to examination, layer by layer, and the following results confirm the above.

That portion of the scale next the iron and nearest the fire contained but traces of  $\text{CO}_2$ , and was principally the hydrated oxides. The middle portion of the scale was a mixture of  $\text{CO}_2$  and the hydrated oxides, while the upper portion of the scale contained carbonates, but no hydrated oxides. In other words, the composition of the scale will depend, in a great measure, upon what portion of the boiler the deposit is made. That deposited on the iron or shell not in contact with the flame or not subjected to extreme heat, will remain as deposited—as carbonates and sulphates, while that scale deposited upon the iron subject to the flame or heat sufficient to drive out any carbonic acid from the scale, will vary in the amounts of  $\text{CO}_2$  and water of hydration as indicated.

Scale formed in which the lime all exists as calcium sulphate and in which no magnesium carbonate is present will be subject to but little variation.

LABORATORY OF ANALYTICAL CHEMISTRY,  
STEVENS' INSTITUTE OF TECHNOLOGY.

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## MILK ANALYSIS.

BY H. DROOP, RICHMOND.

Dr. Davenport has (*Journ. Anal. Chem.* **3**, 309) stated that in his opinion the advantages of his modification of Wanklyn's method have not received due consideration in the discussion of the relative methods of milk analysis (*Analyst* **14**, 121). As the author of that paper, I should wish now to give my reasons for not favorably noticing this method.

Dr. Davenport claims that by the use of large basins the film of milk residue obtained is very thin, and therefore the solvent has no difficulty in extracting the whole of the fat within one-tenth of one per cent. Assuming the density of milk solids to average about 1.5, I calculate from the data given (i. e., that each gram of milk is spread over about one square inch) that the average thickness of the film of milk solids is .005 inch. The average thickness in the unmodified Wanklyn process being .01 inch, or perhaps a little more. the lessening of the thickness by this modification is not very startling. From the data given by Adams (*Analyst* **10**, 46), I calculate that on paper the thickness of the

film of milk solids is less than .00002 inch, and from my own measurements of Kieselguhr, I conclude that the film dried up on this medium is about .0000005 inch, or the one ten-thousandth of the thickness of the film in Dr. Davenport's modification. As I have, as stated in my paper (*loc. cit.*), found that, by passing milk through paper, or through a layer of Kieselguhr, and even, though to a less extent, through sand and other coarse powders, there is almost complete separation between the fatty and the aqueous portions, I consider that the fat is, in the methods to which I have given precedence (i. e., Adams & Kieselguhr), in a far more favorable condition for extraction, than the figures showing the relative thicknesses of the films seem to indicate, the fat being almost wholly freed from the enveloping solids not fat. In direct evaporation there is relatively little tendency for separation of the fat. From these facts, I did not suppose that this method would give anything like the total amount of fat, and therefore rejected Wanklyn's method and its modifications as methods by which a correct analysis may be made. And my theoretical objections were confirmed by experiment. I have tried extracting milk solids evaporated in a platinum dish  $3\frac{1}{2}$  inches wide with slightly rounded bottom, taking as small quantities as 1 gram (giving a thickness of film about one-tenth of that in Dr. Davenport's residues), and in no case could I get within *three-tenths of one per cent.* of the fat given by Adams' process, the average being nearly half a per cent. too low. It will be sufficient to give the figures of the milk in which the difference was the smallest.

Fat by Adams.	Fat by Method just mentioned.	Error.
8.37	8.03	— .34

This was extracted (as indeed were all my experiments) with successive quantities of ether, boiled each time until no more fat could be obtained, as many as twenty portions being frequently used. My results are entirely in accordance with those arrived at by the Milk Committee of the Society of Public Analysts. [I may here state that when using Adams' method, I take the precaution to completely extract the paper, using generally acid alcohol (i. e., alcohol and about 10 per cent. acetic acid) (*cf. loc. cit.*)]. The only difference between the methods is that we used ether and Dr. Davenport petroleum naphtha, which for the purpose of milk

analysis, are identical in their solvent powers. Ether does not, as stated by Dr. Davenport, dissolve milk sugar (*cf.* Hehner, *Analyst* 8, 253). I admit the objection to ether that it slightly dissolves lactic acid, but as this can always be removed by neutralization, this objection is not serious.

I cannot on the above grounds admit Dr. Davenport's modification as a method for the correct analysis of milk, and consider that the results obtained by it are underestimated by about one-half per cent.

KHEDIVIAL LABORATORY,  
CAIRO, EGYPT.

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NOTE BY DR. B. F. DAVENPORT.—I erred on page 310 of my article upon milk analysis published in this journal for last year in referring to milk sugar as soluble in ether. This has been shown by O. Hehner, on page 254, of *The Analyst* for 1883, not to be the case.

I have no doubt but that milk solids dried upon Kieselguhr, or any other very fine light powder, and percolated for several hours as recommended by H. D. Richmond on page 124 of *The Analyst* for 1889 would yield an extract of something weighing a fraction of one per cent. more than a milk fat determined in the manner recommended in my article. In fact, I should expect it to do so. I should expect that some of the fine light powder would be mechanically carried through the percolator, unless further precautions than are mentioned were taken to prevent it, and that it would not be apparent upon inspection. Besides, Henkle in *Molkerei Zeitung* 2, 259, has shown that cows' milk contains upon the average one-tenth of one per cent. of citric acid, which acid is readily soluble in ether. An average cow, he reports, yields in her milk daily as much citric acid as is contained in two to three lemons, and the cows of Bavaria yearly as much as is contained in four hundred million lemons. Furthermore, the peptone, which R. Palm in *Zeitschrift für analyt. Chemie*, 1888, p. 363, declares to average in cows' milk about 1.5%, and to be a solution of albuminoids in lactic acid, would, I should think likely from its reaction with ether as reported by him, be likely to add something to the weight of an ether extract. I can well imagine that these

various extracts might altogether foot up even to the half of one per cent.

The above are some of the reasons why my method of milk analysis has seemed to me more satisfactory than any modification of the percolator method which I have as yet seen proposed with the use of ether as the solvent, for they have all seemed to me to involve a great liability of weighing other matter as fat.

### AN EXAMINATION OF FUSEL OIL.

BY J. H. LONG AND C. E. LINEBARGER.

A few analyses of fusel oil are given in the literature, but of these none, as far as we know, have been made of samples of American origin.

The analysis most frequently quoted is that by Rabuteau, while less complete results are given by others. We have attempted to determine, approximately, the composition of a sample of fusel oil obtained at a Chicago distillery, and give the results below.

Most of our American distillers use corn as the chief substance to be converted into mash, with smaller amounts of other grains, and it would therefore naturally be expected that a somewhat different product would be obtained from that produced by a mash of potatoes or beets.

For the purpose of our investigation, several gallons were secured and submitted to distillation, and the other tests given below. This oil had been separated from alcohol fermented during the spring season, by the longer or 72 hour period allowed by law. When brought to the laboratory, it was saturated with water and held some in suspension. This was allowed to settle out, leaving a perfectly clear liquid, of which the specific gravity was found to be .810 at 20° C. For one series of tests, two liters of this clear oil was dried as thoroughly as possible by shaking it with anhydrous copper sulphate. It was found that all of the water could not be removed in this way. The liquid poured from the sulphate was then treated with dry potassium carbonate, the mixture being kept at a temperature of 40–50° C. for two hours on several successive days. The supernatant liquid was then poured off and distilled nearly to dryness from a retort. Of the

distillate thus freed from the water and purified, a liter was taken for a preliminary fractionation. After three complete fractionations the following approximate results were obtained from this sample :

80- 90° . . . . .	17 cc.
90- 95 . . . . .	8 "
95-105 . . . . .	15 "
105-115 . . . . .	30 "
115-120 . . . . .	55 "
120-125 . . . . .	95 "
125-130 . . . . .	240 "
130-133 . . . . .	515 "
Loss and residue . . . . .	25 "

The general character of the liquid being shown in this way, larger quantities were operated upon, from which we finally secured several liters boiling above 130°, and correspondingly smaller amounts at the lower temperatures.

Attention was first turned to the portions with higher boiling points, and at the outset the specific rotation was found for several different samples. For the fractions boiling at the given temperatures, we found in a 400 mm. tube (Schmidt & Haensch, large model instrument) at 25°C.

Fraction.	$\alpha_D$	$d_{25}$	$[\alpha]$
120-125°	-3.37°	.8075	-1.043
125-128	-3.94	.8092	-1.217
128-130	-3.86	.8110	-1.189
130-133	-3.59	.8115	-1.106

From this it is evident that notwithstanding all our precautions, a considerable portion of the active amyl alcohol passed over below 125° C., with other portions, and this was observed in samples distilled at several different times. An attempt was made to separate the active and inactive alcohols in two of the portions. For this purpose, over a liter of the portion boiling above 130° was treated with sulphuric acid according to the Pasteur method, the mixture of acid and alcohol being allowed to stand for a week, with an occasional gentle heating on the water bath. The barium amyl sulphate was formed in the usual manner, and crystallized repeatedly in fractions, the less soluble portion being finally reserved. This was converted into the sodium salt

by treatment with sodium carbonate. The sodium salt was distilled with sulphuric acid, producing an alcohol which after washing and drying showed a constant boiling point of  $131^{\circ}$  and a specific gravity of .8116 at  $25^{\circ}$ . Only 30 cubic centimeters of the alcohol was obtained in the process. When examined in a 100 mm. polarization tube, it showed a rotation  $a_D = -.18^{\circ}$ , from which the specific rotation  $[\alpha] = -.222^{\circ}$ . This is a smaller value than usually given, suggesting, probably, comparative freedom from the active alcohol. An equal degree of success was not obtained in the separation of the latter in a state of purity. For this a liter boiling below  $128^{\circ}$  was treated in the same manner as before, but only a small amount of alcohol was secured from the more soluble barium amyl sulphate. When washed and dried, the volume amounted to about 20 cc., and showed a boiling point  $128-129^{\circ}$  C. In the 100 mm. tube this gave a rotation  $a_D = -3.50^{\circ}$ , which is a much smaller rotation than reported by Ley, LeBel, and others.

The preparation of this alcohol from the more soluble barium amyl sulphate is practically a very tedious matter, and it is evident that in our experiments the crystallizations were not carried far enough. But enough was done to show that both alcohols were present in quantity in the fusel oil. From a preliminary examination of the oils obtained from other sources, it appears that the amount of the active alcohol present must in some cases be quite small, as the specific rotations of fractions boiling from  $128-133^{\circ}$  were often less than  $[\alpha] = -.75^{\circ}$ .

In the distillation of the dried crude oil in quantity, numerous small fractions could be separated between  $85-105^{\circ}$ , and a considerable portion below  $85^{\circ}$ .

150 cc. of this was converted into bromine compounds in the usual manner, by treatment with red phosphorus and bromine, and the product obtained, amounting to nearly 100 cc., was washed, dried, and carefully fractioned. We found in this way over 50 cc. boiling near  $40^{\circ}$  C. This fraction by subsequent tests was found to consist essentially of ethyl bromide.

35 cc. was obtained boiling from  $61-62^{\circ}$  C., which pointed to the presence of isopropyl alcohol in the liquid brominated. Practically nothing was found boiling above these limits.



From the boiling points of the alcohols taken, it would be possible for butyl alcohol to be present, and this has been reported as a constituent of fusel oils. But we did not succeed in isolating a bromide fraction corresponding to it. The bromide is said to boil at  $72^{\circ}$  C., but only a very minute quantity was obtained about  $62^{\circ}$ .

It appears, therefore, that the lower alcohol fractions consist essentially of the ethyl and isopropyl compounds.

It was stated above that no large fraction of alcohol was obtained between  $85^{\circ}$  and  $105^{\circ}$ . We took the fraction boiling between  $95-105^{\circ}$ , and converted it into bromide as before. If normal propyl alcohol existed in the oil, it should be found in the fraction taken, and as it is readily converted into a bromide, we should expect to find some of the latter compound boiling about  $71^{\circ}$ . In the distillation of the mixed bromides resulting from the reaction, it at first sight appeared that only a trace boiled as low as  $71^{\circ}$ , but after some little difficulty, we found that the mixture could be resolved into two portions, boiling between  $70-73^{\circ}$  and  $90-94^{\circ}$ . That the lower portion actually consisted of normal propyl alcohol, was shown by the behavior of the product on saponification.

The presence of a product boiling between  $90-94^{\circ}$ , would suggest that in the alcohol fraction brominated, along with the propyl compound, some isobutyl alcohol boiling normally at  $108-109^{\circ}$  must have been present. In order to gain more accurate information regarding the isobutyl alcohol apparently present, 150 cc. of the fraction boiling at  $105-110^{\circ}$  was taken and brominated.

The product obtained after washing and drying amounted to 60 cc., of which over 50 cc. boiled at  $90-93^{\circ}$ . An abundance of the isobutyl alcohol was therefore present in this fraction. It was suspected that the higher fractions,  $110-120^{\circ}$ , might also contain a not inconsiderable portion. They were subjected to treatment with phosphorus and iodine, the latter being added very gradually, so as to avoid the loss complained of by Chapman and Smith (*Journ. Chem. Soc.* **22**, 153). 100 cc. boiling at  $110-120^{\circ}$ , and 100 cc. boiling at  $120-125^{\circ}$ , were treated in this way. The yield was satisfactory. On purifying and fractionating the products, we found 65 cc. boiling at  $121-122^{\circ}$ , 20 cc. boiling at  $128-130^{\circ}$ ,

and over 50 cc. boiling between  $140^{\circ}$  and  $145^{\circ}$  C. Below  $120^{\circ}$  and between  $122^{\circ}$  and  $128^{\circ}$  only very small amounts were found. On further fractionating the portion boiling at  $140$ – $145^{\circ}$ , we found that most of it boiled at  $143^{\circ}$ , while a little boiled continually higher. It would appear, therefore, judging from the boiling points alone, that the fractions converted into iodides consisted chiefly of active amyl alcohol and primary iso-butyl alcohol with a smaller amount of normal butyl alcohol.

It may appear singular that so large an amount of iodide with high boiling point was obtained from the alcohol boiling below  $125^{\circ}$ , but it must be remembered that this fraction showed also a marked rotary polarization; in fact, almost as great as with the fraction  $125$ – $130^{\circ}$ . It is also possible that methyl propyl carbinol was present in the fraction  $120$ – $125^{\circ}$ , as its boiling point is only slightly below  $120^{\circ}$ , and the boiling point of the iodide  $145$ – $146^{\circ}$ , but no attempt was made to separate it.

The alcohols of high boiling point seem to pass over readily with those of lower, but from an experiment carried out by us, it appears plain that the fractions boiling above  $125^{\circ}$  are but slightly, if at all, mixed with lower alcohols. We converted about 200 cc. of the fraction  $125$ – $130^{\circ}$  into iodides, and found that of the purified product, only a very inconsiderable portion passed over below  $140^{\circ}$ .

We have made no attempt to find alcohols or other bodies, present in minute quantity only, in the fusel oil examined, but have sought, rather, to show the characteristic features of the oil. From the foregoing, it appears that it consists chiefly of the active and inactive amyl alcohols, probably three-fourths being made up of these bodies. The next most important substance appears to be isobutyl alcohol, and after that isopropyl and ethyl alcohols, with traces of normal propyl and normal butyl alcohols.

Only a very inconsiderable portion of the original fusel oil possessed a higher boiling point than  $133^{\circ}$ . Part of this residue consisted of alcohols, and a part of bodies of an ethereal nature, as shown by simple saponification tests, but the amounts concerned were too small for identification.

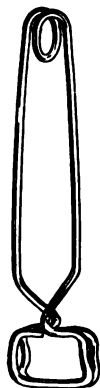
## NOTES FROM THE LABORATORY OF SMITH COLLEGE.

BY J. T. STODDARD.

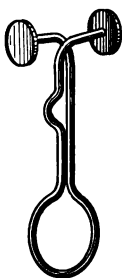
*A New Test Tube Holder.*—The annoyance experienced in using the common wooden test tube holder led me some years ago to attempt to devise a holder which should serve its purpose more perfectly. The wooden holder is clumsy, its rubber band rots and is liable to give way at awkward moments, the peg becomes unglued and drops out, and even in its best estate it holds securely only medium sized test tubes. Tubes of more than two centimetres cannot be inserted sidewise, larger ones are not taken at all, and a separate holder must be used for small test tubes and ignition tubes.

The new holder has been in use in my laboratory for four years now, and has given such good satisfaction that I venture to call attention to it in a form recently somewhat improved. It is made of brass wire, and opens by pressure on the straight sides of the handle; its jaws open to the width of 5 cm., and it holds firmly any tube from 5 mm. up. It thus serves for ignition tubes as well as for all sizes of test tubes.

I have recently had a larger size made of stiffer wire for the purpose of holding flasks, etc. It proves very convenient as a holder of wash bottles when one is washing with boiling water, and also for holding beakers when decanting hot solutions. Both sizes are furnished by the Victor Manufacturing Co., Northampton, Mass.



*A Modified Form of Pinchcock.*—As is shown in the cut, the modification consists in making a side bend in one of the limbs and omitting the double wire which serves as a guide in the ordinary form. The pinchcock can be opened by springing the limbs apart, and thus is readily put on a tube connected at both ends without breaking connections; and when placed so that the tube lies in the side bend leaves the tube open while retaining its place. The side bend was suggested by a note in *Ztschr. anal. Chem.* 24, 399.



*Filtration under Pressure.*—The introduction of this method of rapid filtration into my qualitative laboratory, has resulted in a

very considerable gain in the amount of work accomplished by the class in the time at its disposal. A quarter-inch iron pipe connects each place with a Chapman's aspirator, the pressure being regulated for the whole system by connecting at one point a side neck tube containing mercury, and having a tube open to the air thrust through the cork to a proper distance below the surface of the mercury. The use of brass gas cocks on the exhaust pipe is not to be recommended, as they are affected by the ammonia and other gases which escape from the filtrates, and soon turn hard and often stick fast. A pinchcock on the tubing used to connect the filtering flask is an efficient substitute, but it is better to use it only during working hours and to relieve the rubber tubing from its pressure at the close of work, plugging the tube with a short piece of glass rod. By treating the filter papers with nitric acid of sp. gr. 1.42, as proposed by Francis (*Ztschr. anal. Chem.* **26**, 351), the use of platinum cones is rendered unnecessary, and the paper is in much better condition for the removal of precipitates. In this connection, I wish to call attention to the remarkable efficiency of the Chapman aspirator. I have used an inch aspirator for three or four years, in place of the ordinary air pump, for exhausting receivers, etc., in my lectures, and find it not only gives a high vacuum (the residual pressure being that of aqueous vapor at the temperature of the water running through the aspirator), but works with great rapidity. With our water pressure of about 70 pounds, a receiver of 3600 cc. capacity is exhausted to the above limit (at this season about 10 mm. of mercury) in a minute and a half.

NORTHAMPTON, MASS., Dec. 24, 1889.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.  
COMMUNICATED BY PROF. G. C. CALDWELL.]

## VII. SOME MODIFICATIONS OF THE METHOD FOR DETERMINING CRUDE FIBER.

By W. A. WITHERS.

With the method now in use for determining crude fiber (*Vide Bul.* 19, 1888, *U. S. Dept. Agric.*) there is little trouble in the manipulation except in cases of feeding-stuffs in which the percentage of albuminoids is rather large. In all such cases, however, the albuminoids precipitated by the treatment with sulphuric

acid seriously impede the filtration, rendering it very slow, and from this longer contact a part of the crude fiber may perhaps be dissolved.

This difficulty can be obviated by treating the substance with the sodium hydroxide solution before, rather than after, the treatment with sulphuric acid solution. To test this modification, I compared it with the ordinary method on samples of timothy hay and cotton-seed meal. In both cases clear filtrates were secured by the modification in from 15 to 30 minutes, while with the ordinary method the filtration with the hay required about the same time, but the cotton-seed meal from 18 to 24 hours. With timothy hay the two methods gave practically the same results. With cotton-seed meal the ordinary method gave 2.68% and 2.91%—average, 2.80%; while the modification gave 3.63, 3.58, 3.69, 3.49 and 3.44%, an average of 3.57%.

The determinations on hay show that the modification gives reliable results. In the case of cotton-seed meal, we see that by the ordinary method .77% of crude fiber was dissolved by the ordinary method, possibly on account of the slow filtration, being more than 20% of the whole amount.

For accuracy and, therefore, agreement of results, as well as time saving, the modification seems to recommend itself.

*Rapid Filter.*—The asbestos filter gives good results if covered with a layer of glass wool. Care should be taken, however, not to add too much liquid at a time, as this may cause the glass wool to become displaced. The coarser asbestos gives the best results. Ladd (*N. Y. Ex. Sta. Rep.*, 1887, p. 378) finds that when the asbestos filter is returned with the residue, a larger per cent. of fiber is found, and the two reasons given are that it prevents so thorough contact, and that it necessitated lowering of temperature to prevent bumping. When, however, the substance is first treated with alkali, there is no tendency to bump with the acid treatment, and consequently there is no need of lowering the temperature. As to how much the first mentioned cause will affect the results, I have not tested.

*Prevention of Frothing in Boiling.*—This can be done by directing a moderate blast of air into the flask through a small glass tube (1.5 mm. diam). The constant level of the liquid can be

maintained by adding boiling water from time to time, or by using a reflux condenser.

### VIII. THE DETERMINATION OF CRUDE FIBER.

BY W. A. WITHERS.

This work was begun to ascertain, if possible, some of the discrepancies in results obtained by different chemists for crude fiber.

The samples used were timothy hay and cotton-seed meal. They were not extracted with ether previous to treatment with acid and alkali. Except when so stated, the solutions were  $1\frac{1}{4}\%$   $\text{H}_2\text{SO}_4$  and  $1\frac{1}{4}\%$   $\text{Na}_2\text{O}$ , the time of boiling 30 minutes, and the results, in per cent., calculated on the dry sample.

The following questions were considered :

#### 1. Amount of $\text{Na}_2\text{O}$ neutralized.

By titration before and after treatment, an average of five different determinations gave an equivalent of .114 gms.  $\text{Na}_2\text{O}$  neutralized by timothy hay for every gram of substance taken, showing that only a very small portion of the  $\text{Na}_2\text{O}$  added enters into chemical combination, and part of this is from saponification of the fat, which in regular analysis would have been extracted with ether.

#### 2. Sulphuric acid neutralized.

Residues from timothy hay, after treatment with  $\text{Na}_2\text{O}$  solution, were taken. It was found that for each gram of substance originally taken .01 gm. of  $\text{H}_2\text{SO}_4$  was neutralized, showing that the sulphuric acid does not enter into chemical combination at all.

3. Effect of different strengths of  $\text{Na}_2\text{O}$  solution. This was tested on timothy hay with the following results :

	Time of Treatment.			
	45 Minutes.		1½ Hours.	
$\text{Na}_2\text{O}$ (grams) used per gram of substance . . . . .	2.34	1.27	1.27	1.00
Residue, per cent. . . . .	{ 33.67	35.26	{ 33.34	35.06
	{ 33.28	35.36	{ 33.70	35.30
	{ 33.88		{ 33.88	
Average . . . . .	33.48	35.31	33.64	35.18
Difference due to different strengths of solution . .	1.83		1.54	

This shows that the stronger the solution, or the more used of

the solution of the same strength, the smaller will be the per cent. of fiber.

#### 4. Effect of time in treatment with $\text{Na}_2\text{O}$ solution.

In the filtrations, a simple asbestos filter was used. After boiling the substance for 30 minutes, the residue, after drying and weighing, was detached from the filter as completely as possible, and subjected to another similar treatment with a new portion of the reagent. This method avoids very largely the errors of analysis that would occur had different samples been taken and tested for different periods of time. Duplicate determinations *A* and *B* were made.

Treatments with Alkali.	TIMOTHY HAY.				COTTON-SEED MEAL.			
	<i>A.</i>		<i>B.</i>		<i>A.</i>		<i>B.</i>	
	Resi- due.	Dis- solved.	Resi- due.	Dis- solved.	Resi- due.	Dis- solved.	Resi- due.	Dis- solved.
1	36.96	63.04	36.21	63.79	4.46	95.54	4.66	95.34
2	33.49	3.47	32.79	3.42	3.95	.51	4.14	.52
3	31.85	1.64	31.17	1.62	3.26	.69	3.47	.67
4	30.53	1.22	29.82	1.35	2.99	.27	3.09	.38
5	29.74	.79	29.03	.79	With $\text{H}_2\text{SO}_4$			
6	28.78	.96	28.34	.69	2.39	.60	2.41	.68

These treatments represent about 50 minutes contact with the alkali, being about 10 minutes to raise to boiling, 30 minutes boiling, 5 minutes standing, and 5 minutes filtering. The first treatment required from 10 to 15 minutes in filtering, thus making the contact longer. In the case of timothy hay, therefore, this difference is about .07% of fiber per minute, and of cotton-seed meal .01%.

#### 5. Effect of time in treatment with $\text{H}_2\text{SO}_4$ solution.

The residue, after treatment with alkali, was treated in the same way as above. Timothy hay was taken.

	<i>A.</i>		<i>B.</i>		<i>A.</i>		<i>B.</i>	
	Resi- due.	Dis- solved.	Resi- due.	Dis- solved.	Resi- due.	Dis- solved.	Resi- due.	Dis- solved.
From $\text{Na}_2\text{O}$ Treatment,	34.70	65.30	33.92	66.08	28.78	71.22	28.34	71.66
With Acid, 1	29.10	5.60	28.33	5.59	25.59	3.19	25.38	2.96
2	28.20	.90	27.60	.73	24.79	.80	24.73	.65
3	27.81	.39	27.25	.35	23.91	.88	24.08	.65
4	27.32	.49	26.78	.47				

The time of contact with acid was about 40 minutes, which

makes a difference of nearly .02% of fiber for every minute of treatment with acid. Ladd (*5th An. Rep. N. Y. Ex. Sta.*) has shown that the degree of heat employed causes a difference in results. The above work shows that differences are also due to the amount and to the concentration of the different reagents used and to the time of contact. To secure agreement in results, therefore, uniformity in all those conditions must be attained. Granting that this can be done, the question of accuracy of results confronts us. Without going into a review of the work of different chemists bearing on this point, let me call attention to the above tables under 4 and 5. One of two conclusions must be drawn from this work, viz.: 1st, That if half an hour treatment with each alkali and acid is sufficient to give the per cent. of crude fiber, then crude fiber is soluble in both acid and alkali, as is shown above by further treatment, and that to a somewhat considerable extent; or, 2d, That if crude fiber is not soluble in these reagents, then six treatments with alkali and three subsequent treatments with acid are not sufficient to separate it.

Either of these conclusions is sufficient to discredit the method as wanting in accuracy, and being at best only a rapid method of approximation to the truth.

#### 6. Ash in the residue.

Six samples were taken for this:

2	with alkali	45 minutes	and acid	1 hour.
2	"	"	1½ hours	" " ½ "
2	"	"	1½ "	" " 1 "

In no case was any ash found in the residue.

#### 7. Nitrogen in the residue.

The albuminoid equivalent of this was found to vary from .4% to .5% after one treatment with alkali. The acid did not remove any more, but subsequent treatments with alkali left no nitrogen.

## ILLUSTRATIONS OF SEWAGE DECOMPOSITION IN STREAMS.

By J. H. LONG.

During the last four years I have had occasion to carry out a lengthy investigation on the question of pollution of streams in Illinois, and in the progress of the work have observed certain



points which I consider of interest to chemists dealing with analytical problems of similar nature.

This work was undertaken by authority of the State Board of Health, and since its beginning I have examined nearly 1000 samples. The results reached in a preliminary examination were presented to the Board in 1887. A few of them were explained in a paper in the *American Chemical Journal*, Vol. X, No. 1, while the methods employed and tabulated results of the whole will appear in a future annual report of the Board.

The largest part of the work consisted in a study of the Illinois river from its sources to its mouth, and it is only with this part of the subject that I have to deal here.

At all seasons of the year the upper Illinois river receives a good part of its water from Lake Michigan through a canal flowing southwest from Chicago to Joliet, when a union with a small stream known as the Des Plaines river is made. A few miles further toward the southwest these waters are joined by those from the Kankakee and Du Page, thus forming the Illinois proper. The watershed separating the basin of Lake Michigan from that of the Mississippi is very low, and is but a few miles from the lake. The canal referred to is fed by pumps, the water being drawn through the city and discharged by these pumps toward the west at the rate of 50,000 cubic feet per minute. The water in going through the city receives about three-fourths of its sewage, and in the canal flows undiluted to Joliet, a distance of 33 miles.

It will be seen, therefore, that we have here a most interesting problem. We have given a stream, highly contaminated at its source, and are able to follow and measure changes in the amount of contamination for many miles. In my first series of experiments, completed during the summer of 1886, very curious and important results were obtained. That season was unusually warm and dry, the rainfall in the part of the state under consideration being the lowest recorded in 15 years, and it was therefore possible to measure changes in the flowing river water, undisturbed by dilution of rain.

In the tests of that season, the determinations made were free and albuminoid ammonia and oxygen consumption by the

Kubel method. The following mean results were obtained, expressed in parts per 1,000,000.

	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.
Bridgeport . . . . .	17.44	1.195	20.58
Lockport, 29 miles . . . . .	10.23	.669	11.30
Joliet, 33 " . . . . .	6.93	.408	7.79
Ottawa, 81 " . . . . .	0.382	.237	5.57
Peoria, 159 " . . . . .	0.035	.187	4.85

Between Bridgeport and Joliet the dilution was practically zero during the whole season. Between Joliet and Ottawa the Illinois receives the waters of the Kankakee, Du Page and Fox, so that at the last named place it was estimated that the canal water was reduced to 43 per cent. of the whole. But as a part of the diluting water came from a marshy region, it was by no means free from organic matter. Besides, some town drainage entered the stream between the two places. It is, therefore, probable, that a reduction in organic matter took place between these points. The proportion of canal water, in the whole, was but slightly changed between Ottawa and Peoria, while some drainage entered at the town of LaSalle. We can trace, therefore, a very remarkable decrease in organic matter between the contaminated source at Bridgeport and the city of Peoria. From a study of all the facts bearing on the case, I have held that this change was due chiefly to oxidation (using this term in the broad sense to include changes brought about by microorganisms) rather than to sedimentation.

During the following winter these mean results were obtained, expressed in parts per 1,000,000 :

	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.
Bridgeport . . . . .	9.7	3.7	22.4
Joliet . . . . .	6.5	2.2	11.3
Ottawa . . . . .	4.7	.75	9.0
Peoria . . . . .	1.7	.43	6.45

In this table the increased amount of albuminoid ammonia with smaller amount of free ammonia at Bridgeport is apparent, and is, of course, due to the fact that decomposition is slower at a low temperature, and hence the sewage reached the pumps in a less advanced stage of oxidation. The large amount of albumi-

noid ammonia at Joliet is worthy of note at a time when sedimentation could accomplish the best results. The very slow decrease in free ammonia must also be noticed.

As intimated above, these tests may be considered as preliminary to a more complete investigation begun May 1st, 1888, and concluded in March, 1889. In this investigation water was collected once a week at the following places between the source of supply at Chicago and the Mississippi river: Bridgeport, Lockport, Joliet, Morris, Ottawa, LaSalle, Henry, Peoria, Pekin, Copperas Creek, Havana, Pearl, Beardstown and Grafton, the last being at the mouth of the Illinois river. Parallel tests were also made of the water supplied by the various tributaries of the Illinois to determine the nature of the dilution. In this investigation, in addition to free and albuminoid ammonia and oxygen consumption, total solids, suspended matter, nitrates, chlorides, and hardness were determined. In the following table only those data important for the present purpose are given and for places where water was regularly collected. During the early part of the season the rainfall throughout Illinois was heavy, in consequence of which the streams were full at times, adding much to the dilution of the main river.

The amount of this dilution can be roughly estimated from the chlorine determinations along the main stream and in the tributaries.

*Mean Results of Analyses. May to October, 1888, inclusive.*

IN PARTS PER MILLION.

Places.	Nitrogen in Nitrates and Nitrites.	Chlorine.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.
Bridgeport . . . . .	.000	46.811	12.253	2.558	23.113
Lockport . . . . .	.000	46.120	10.882	1.990	16.230
Joliet . . . . .	.000	43.658	8.932	1.681	14.301
Morris . . . . .	.380	32.149	4.107	.707	10.920
LaSalle . . . . .	1.037	19.717	.636	.526	8.558
Henry . . . . .	.683	17.660	.467	.481	8.657
Peoria . . . . .	.8915	12.358	.210	.522	9.769
Pekin . . . . .	.795	16.152	.645	.650	9.410
Havana . . . . .	.731	11.583	.342	.430	8.142
Beardstown . . . . .	.62	7.524	.202	.380	7.354
Grafton . . . . .	.582	9.205	.095	.483	7.300

*Mean Results of Analyses. January to March, 1889, inclusive.*

IN PARTS PER MILLION.

Places.	Nitrogen in Nitrates and Nitrites.	Chlorine.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.
Bridgeport . . . . .	.000	62.934	8.925	2.806	26.502
Lockport . . . . .	.000	56.083	8.149	2.489	22.820
Joliet . . . . .	.000	57.717	8.488	2.666	21.717
Morris . . . . .	.000	28.748	47.16	1.587	10.696
LaSalle . . . . .	.942	13.105	1.456	.637	8.582
Henry . . . . .	.962	11.691	1.059	.404	8.626
Peoria . . . . .	.510	12.860	1.637	.549	9.611
Pekin . . . . .	1.259	11.792	1.591	1.015	13.358
Havana . . . . .	.414	9.277	1.078	.585	9.234
Beardstown . . . . .	.966	6.933	.762	.357	5.505
Grafton . . . . .	.087	7.523	.875	.722	9.818

In explanation of some of the peculiarities of the above tables, it must be stated that while the rainfall during 1888 was much heavier than during 1886, the mean temperature was in a marked degree lower. The winter of 1888-'89 was, however, much milder than that of 1886-'87.

In comparing the summer tests of 1886 with those of 1888, we notice that at Bridgeport in the first named year the free ammonia was much higher and the albuminoid ammonia much lower than during the second season. It is also clear that the rate of change in these products between Bridgeport and Joliet is different for the two seasons. I think this can be largely looked upon as an effect of temperature, as dilution, contamination and agitation of water were practically the same within these limits through the two seasons. During the hot summer of 1886 much greater decomposition must have taken place in the Chicago sewers themselves than during the cooler one of 1888, so that in the first case the diluted sewage reached the pumps in a more advanced stage of oxidation than in the latter.

One would expect to find, under these circumstances, less free ammonia and more albuminoid than in a season when the oxidation conditions had been more favorable.

To follow the change in the sewage after it leaves Chicago in its flow toward the Mississippi, we must consider the character of the diluting water from the tributaries. The mean results ob-

tained by analysis of these waters are given here, in parts per million, as before.

	Nitrogen in Nitrates and Nitrites.	Chlorine.	Free Ammonia.	Albuminoid Ammonia.	Oxygen Consumed.
DuPage River, enters above Morris . . .	.307	5.786	.417	.346	4.743
Kankakee River, en- ters above Morris .	.094	1.015	.114	.585	12.661
Fox River, at Ottawa, above LaSalle . . .	.027	4.974	.278	.463	7.066
Big Vermillion Riv., at LaSalle, ab. Henry	3.348	5.461	.129	.341	6.914
Sangamon River, above Beardstown .	.755	3.609	.053	.285	5.480

The flow from the DuPage is very small during the summer and its effect on the Illinois can be left out of consideration.

The Kankakee, draining a marshy country, has a steady flow throughout the summer and forms about 20 per cent. of the Illinois water at Morris. Its character is shown by low chlorine and nitrates and high albuminoid ammonia and oxygen consumption. Between Morris and LaSalle the Fox enters and dilutes the Illinois largely, as indicated by the decrease in chlorine. The dilution by the Big Vermillion is not large. The high nitrates here are worthy of interest. The city of Streator and several coal mines drain into the stream. Below Peoria the tributaries of importance are the Sangamon and Spoon. I have no data for the latter, but the results for the Sangamon are given above. Perhaps 30 per cent. of the flow at Beardstown comes from these two streams.

Aided by these data, we can now consider the main river. Between Bridgeport and Lockport, a distance of 29 miles, there is during the summer an evident disappearance of organic matter, as shown by change in the free and albuminoid ammonia and oxygen consumption. But during the winter the change is in a marked degree less. This is especially apparent if we notice that the chlorine tests during the winter show some dilution between the two places. From Lockport to Joliet the distance is four miles, but on its way the water passes through four locks and over two dams to point of collection. It is thus thoroughly agitated and aerated. During the summer the tests show a decrease in organic matter, but the winter examinations indicate, apparently, an increase,

as shown by albuminoid ammonia. A slight increase in free ammonia is also found. These observations are of practical importance. They show, first, that at Lockport the decomposing matter was not yet in condition to respond most perfectly to the albuminoid ammonia test, and also that the free ammonia gradually produced had accumulated rather than decreased by fermentation. Dilute solution of white of egg undergoing putrefaction yields its largest amount of albuminoid ammonia at the start, as shown by experiments carried out in my laboratory by Mr. Powers. (See Oct. 1889, number of this Journal.) But it is conceivable that solids in suspension, or other nitrogenous matters more stable than white of egg, would yield their largest amount of albuminoid only after preliminary disintegration.

Between Joliet and Morris the distance is 22 miles, and on the way there is a dilution of about 20 per cent. by water in which the numbers for albuminoid ammonia and oxygen consumption are high. A part of the drainage of Joliet enters here besides. Giving these points due weight, it will be seen that there is a large reduction of organic matter in this part of the stream during the summer. This is not chiefly due to sedimentation. It has been shown by engineers in charge of surveys along the Illinois river, that owing to sufficiently high velocity of the water, sedimentation does not take place here. During the winter the relative dilution from the Kankakee was much greater, about half the water at Morris coming from the last named stream. When the character of the diluting water is remembered, it is plain that the nitrogenous matter has suffered no change between the two places. In the 37 miles between Morris and LaSalle there is a great decrease in free ammonia with increase of nitrates, but when the dilution of the Fox river is considered, it is plain that the change in albuminoid ammonia is not important. During the winter season the Fox river dilution was relatively greater, which lessens somewhat the apparent decrease in albuminoid ammonia at this time. It is true, however, that changes take place in this part of the river which in the warmer season took place above.

In the 28 miles between LaSalle and Henry no important changes have taken place.

At Peoria the river widens into a lake, which receives a por-

tion of the drainage of the city. The point where the samples were taken for analysis was evidently not beyond the influence of this contamination. During the winter this was increased by the drainage from sheds at the distilleries at which 25,000 head of cattle were fed. The effect of this is shown in the Peoria water, but most clearly in that from Pekin, ten miles below. Especially interesting is the great increase in nitrates observed at this point, and after the addition of *fresh* contamination.

Between Pekin and Beardstown there is a gradual improvement in the river, as shown by both summer and winter tests. Below Beardstown the Illinois was often diluted by back water from the Mississippi, which made the result of analysis irregular and obscure.

From the above it is apparent that while a gradual loss in organic matter occurs all the way between Bridgeport and Peoria, the rate of change was far less rapid in the summer of 1888 than in that of 1886. This difference, I believe, is chiefly due to differences in temperature and rainfall, which act directly and indirectly to modify the rapidity of bacterial oxidation.

In a wet summer the contents of the Chicago sewers, besides being cooled by rainfall, are rapidly washed out into the canal leading to the pumps. In a season of little rainfall much matter remains long enough in the sewers to become greatly modified by decomposition and consequently disappears rapidly when thrown into the main channel. These opposite conditions were illustrated in the summer seasons in which tests were carried out, and they doubtless can be duplicated in all large cities in which the sewers are built with but slight incline. Sedimentation cannot play a more important part in the apparent purification of these waters in summer than in winter. In fact, after the navigation of the canal closes in the early winter, precipitation can take place which was impossible during the warmer months. Yet the winter tests show practically no decrease in the organic matter between Bridgeport and Morris. It would appear, therefore, that the self-purification of a very cold water is a slow process, even when aided by sedimentation.

On the other hand, the very remarkable results obtained be-

tween Bridgeport and Joliet in our first season's work show that with a sufficiently high temperature the disappearance of organic matter may be very rapid, unaided to any great extent by sedimentation.

It is known that temperature differences of a few degrees make very important differences in the rates of bacterial multiplication in many cases, and consequently in their efficiency as filth destroyers, and giving proper weight to this fact, I think many of the discrepancies observed between different examinations of the same polluted water, made at different times, may be explained.

The appearance and increase in nitrates and nitrites in the Illinois river affords us an instructive illustration. Frankland and others have shown that they are not formed in fresh sewage, and we see here that they appear only after a flow of many miles.

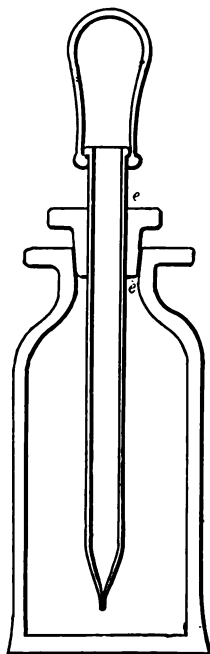
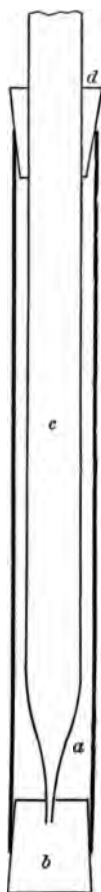
With the slower disappearance of albuminoid ammonia and less abundant formation of free ammonia in the cold season, we notice the later appearance of nitrates and nitrites. Investigation may show that the appearance of these compounds marks an important stage in the purification of a polluted stream.

It is probable that they are produced only after practically all the readily fermentable bodies have been more or less changed, as in presence of such matter denitrification can take place with destruction of nitrates, and evolution of nitrogen even. The greatly increased nitrates below Peoria after pollution by fresh drainage from the cattle sheds would seem to disprove this view. But such drainage is rich in hippuric acid, and this body, as well as its derivative, glycocoll, is readily broken up. Besides, because of the comparatively simple nature of the cattle feed (distillery slops and hay), the other matters present here must be less complex than what we have in ordinary city sewage, and therefore sooner converted into ammoniacal and other simple compounds.

Investigations, such as I have given an outline of above, are very difficult because of the practical impossibility of controlling all the conditions of experiments. Irregularities creep in where least expected, and in consequence the results of single observations have but little value when taken alone.

The results of investigations extended through a season have a different value, and I believe we can draw conclusions from these ex-





periments on the Illinois which can be applied to the study of polluted river waters in general.

CHICAGO, January, 1890.

### PIPETTE FOR HYDROFLUORIC ACID.

BY G. P. VANIER.

A convenient pipette for HF may be made from ceresine in the following manner: pour melted ceresine (one of Baker & Adamson's ceresine bottles) into a mold which may be made in the following way: Roll a piece of paper into a tube (*a*) about  $\frac{3}{8}$  in. diameter, placing a cork (*b*) in one end. Into this tube place a glass tube (*c*) drawn out at one end, the latter being kept in place by forcing the pointed end into the cork (*b*) and by the use of three small wooden wedges at the top. The cut represents the pipette applied to one of Baker & Adamson's ceresine bottles of HF, a hole being cut through the stopper, which is then cemented to the pipette at (*e*) by a hot iron.

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#### DETERMINATION OF "TOTAL RESIDUE" IN WATER ANALYSIS.

By WM. P. MASON.

Water residues, particularly those from mineral waters, are often so hygroscopic as to be exceedingly difficult to weigh, if the evaporation be performed in an open platinum dish. It has been my custom, for some time past, to substitute for the dish a large broad weighing bottle, of ordinary form, holding somewhat more than 100 cc. The vessel being closed after dryness is obtained, the weighing may be done at leisure. Results are more satisfactory, but great difficulty is found in afterwards removing the stopper of the bottle, owing to the high temperature at which it was closed.

To overcome this objection, I have had bottles made with a small stop-cock in place of the usual handle on the cover, and am thus able to control the inside pressure. Such bottles may be obtained of Eimer & Amend, New York.

RENS. POLY. INST. Troy, N. Y.

# ABSTRACTS.

## APPARATUS AND REAGENTS.

**A Simple Substitute for Kipp's Apparatus.**—Eustace Thompson, Chem. News **60**, 228.

The flask *A* (capacity about 500 cc.) contains HCl. A bottle *B* contains chips of marble. *A* and *B* are connected by a tube in the form of a siphon reaching to the bottom of each. A short bent tube is also inserted through the cork of *A*. When in use, the tap on *B* is opened, and acid is forced through *A* into *B*, and by a little care the supply of carbonic acid may be easily regulated. Zinc or ferrous sulphide may be substituted for the marble chips, for the preparation respectively of hydrogen and hydrogen sulphide. An advantage which this simple substitute has over Kipp's apparatus is that it requires far less acid, and the unsaturated portion of acid does not mix readily with that which has performed its office and formed chlorides with the bases used

A. H. W.

**Magnesium as a Reagent.**—H. N. Warren, Chem. News **60**, 187. Attention is called to the high reducing properties of this metal. Its freedom from arsenic suits it well for the elimination of pure hydrogen in Marsh's test. Absence of iron renders it valuable in reducing ferric salts for titration. Its ready precipitation of zinc in solutions distinguishes it from all the other metals. Its behavior with iron salts is more complex, but iron may be entirely separated by it from a solution of a chromic salt; e. g., take an acid solution of chromeisen, neutralize with sodium carbonate, and redissolve in a small amount of acetic acid the precipitated carbonate. If now one gram of magnesium is added, the ferric salt is reduced almost instantly, and on the application of heat the liquid changes from the deep green characteristic color of chromium chloride through pink, red, violet, to a pure green,

its original tint, while the iron is precipitated upon the magnesium in a somewhat coherent form, frequently contaminated with oxide. This is then withdrawn from the solution containing chromium, boiled with a few drops of  $\text{HNO}_3$  and tested for iron by potassium sulphocyanide. As a reagent in the dry way, magnesium reduces all metals but those of the alkaline earths and alkalis, and even refractory substances as silica and boric anhydride may be almost instantly reduced when intensely heated in closed vessels with the same. Fused with molybdic anhydride, it attacks it in a violent manner.

A. H. W.

**A Water Jacketted Flexible Tube.**—Frederick J. Smith, Chem. News 60, 187. A length of small rubber tubing is drawn through another of equal length but greater diameter. Each end is furnished with a piece of glass tubing which fits the smaller tube. One end is bound with cord, and after the space between the inner and outer tubes is filled with water, or any liquid required, the other end is then bound, forming a satisfactory water-jacketted flexible tube.

A. H. W.

**An Improved Soxhlet Extractor, and Apparatus for Distilling in a Vacuum.**—J. Lewkowitsch, Journ. Chem. Soc. 1889, 359. The improvement consists in attaching a stop-cock to the small glass arm for return of liquid to the lower part of the apparatus, so that small portions of the liquid used for extraction may be removed during the operation to determine the completeness of the extraction, without discontinuing the process or disconnecting the apparatus. The other pieces of apparatus are best understood by seeing the cuts.

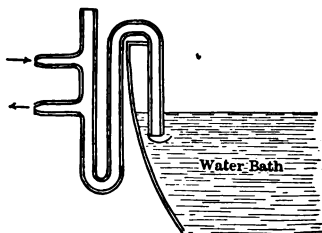
C. W. M.

**Standardization of Silver Solution.**—Herman Alt, Chem. Zeit. 13, 1376. Instead of hydrochloric acid, the author uses pure barium chloride ( $\text{BaCl}_2 + 2\text{H}_2\text{O}$ ) for standardizing silver solution. A weighed amount of barium chloride is dissolved in water and an equivalent amount of pure zinc sulphate is added to convert the barium into the sulphate. A slight excess of the latter salt does no harm. A few drops of potassium chromate solution are then added and the solution titrated with silver nitrate. The end reaction is very sharp, and is not affected by the small amount of chromate of zinc which is formed during the operation.

s. c.



**A Simple Water-Bath Regulator.**—T. H. Easterfield, Chem. News **60**, 250. The apparatus represented consists of a glass tube, open at both ends, bent twice parallel to itself, and having two side-tubes sealed into the longest limb, the upper side-tube being for admitting the water supply, the lower for the overflow. When the tube is once filled with water, by turning on the water supply and closing the overflow tube for a moment, the apparatus acts as a continuous syphon and keeps the water-level constant. A. H. W.



**Purification of Hydrofluoric Acid for Use in Analysis of Silicates.**—Robert Hamilton, Chem. News **60**, 252.

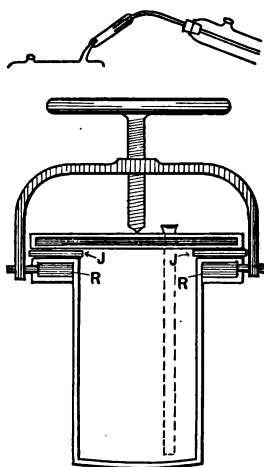


Fig. 1.—Arrangement of Nose of Retort for Distilling Hydrofluoric Acid.

Fig. 2.—Leaden Retort for Distilling Hydrofluoric Acid.

R, wrought iron ring  $1 \times \frac{3}{8}$  in.;  
J, India rubber joint.

The body of the retort is 6 inches long by 4 in. diameter, of heavy sheet-lead, and having a broad seat formed for the India rubber joint J by beating the lead back over the iron ring R. Two projections from opposite sides of the ring secure the ends of the iron bridge (1 inch wide by  $\frac{3}{8}$  inch thick) which is the main feature of the retort. The lid is made of  $\frac{1}{4}$  inch iron plate covered with lighter sheet-lead, and all the lead joints are burned.

The leaden nose of the retort points upward, and the India rubber tube is carried a little higher to prevent any dissolved lead being carried along. Thin-walled, black India rubber tubing (3–16 inch bore) connected with the leaden nose by stouter tubing of larger bore and passing through India rubber corks in ends of Liebig's condenser case, is the arrangement for condensing. As the crude strong acid rapidly destroys the tube, it should be diluted till it contains about 25 per cent. HF. After first charging the end of the India rubber tube is dipped beneath water until silica ceases to separate.

A. H. W.

**A New Gas-Burner for Laboratory Use.**—M. Gröger, *Ztschr. angew. Chem.* **89**, 639.

A cap, with a conical opening, is fitted on the top of the burner, a cone is so arranged that it can, completely or in part, close the aperture, allowing an amount of gas to pass through sufficient for the flame required. The author gives figures which fully illustrate the apparatus.

J. E. W.

**The Use of Oxygen in Quantitative Analysis.**—W. Minor, *Ztschr. angew. Chem.* **89**, 671.

**Method and Apparatus for Determining the Igniting Point of Explosives.**—Dr. Bein, *Ztschr. angew. Chem.* **89**, 667.

The method consists in heating the material, in an oil-bath, until it ignites and observing the temperature. An illustration is necessary to show the arrangement of the apparatus.

J. E. W.

**An Apparatus for Shaking Liquids.**—A. Stutzer, *Ztschr. angew. Chem.* **89**, 640.

**Apparatus for the Electrolytic Determination of Metals.**—Dr. L. C. Levoir, *Ztschr. anal. Chem.* **28**, 63.

The author calls attention to the fact that it is necessary that solutions to be electrolyzed should be perfectly mixed and claims that many failures to get correct results are due rather to this mechanical cause than to a chemical one. The apparatus described consists of a platinum dish, containing the solution, resting on three metal buttons connected with positive pole of the battery. A similar smaller dish of platinum fits inside this dish and is suspended by three platinum wires connected with a heavier wire, which bends over and rests in a cavity containing mercury. This cavity is in a support capable of being raised and lowered which is connected with the negative pole of the battery. When in position the bottom and sides of the smaller dish are about 3 cm. from those of the dish containing the solution, the solution being of course between the dishes. The bubbles of oxygen gas separated on the walls of the lower dish rise through the liquid and mix the solution thoroughly, bringing every part of it in contact with the negative electrode. The entire separation of the metal is easily and quickly made.

A. A. B.

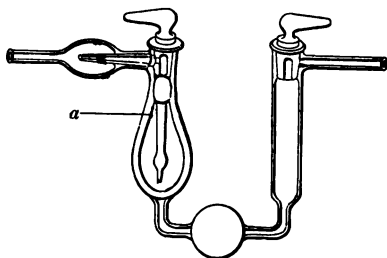
**Contributions to Gas Analysis.**—W. Thörner, *Ztschr. angew. Chem.* **89**, 641.

The author describes several absorption pipettes in which he has modified the usual form used by Hempel; also the application of a water jacket to the burette.

The paper contains a set of valuable tables for the reduction of the volume of  $\text{CO}_2$  at any temperature from  $7^\circ$  to  $30^\circ$  C. and between 736 mm. and 780 mm. pressure to weight. J. E. W.

**A Substitute for the Chloride of Calcium Tube in Ultimate Analysis.**—Jos. Preusser, *Ztschr. anal. Chem.* **28**, 322.

The apparatus described in the *Ztschr. anal. Chem.* **23**, 515, by S. Schmitz, has, according to the author, the disadvantage of



bringing the products of combustion in contact, first, with the phosphoric anhydride, and afterwards with the sulphuric acid, thus expending the more expensive reagent first. It is not possible, owing to the construction of the tube, to simply reverse it and pass the products

of combustion through the sulphuric acid first; and therefore the tube constructed as shown in the cut, is proposed. In this tube the leg containing the sulphuric acid, through which the products of combustion pass first, is blown a little more convex than in Schmitz's tube to give more space to the internal cylinder, which has a bulb at the base. Into this internal cylinder is fused a tube which carries the gas nearly to the bottom of the bulb, whence it issues through the sulphuric acid, reaching the external space through the small opening at *a*. From here it passes through the bulb, connecting the two legs of the tube into the space containing the phosphoric anhydride. The greater part of the water is thus absorbed by the sulphuric acid, and the phosphoric anhydride lasts much longer than it would otherwise. When the sulphuric acid becomes diluted, it is removed by passing through the small tube a pipette, drawn out very thin, and sucking up the acid. A fresh supply of strong acid is introduced by the pipette.

A. A. B.

**Easy Method of Preparing Chromic Chloride.**—A. Vosmaer, *Ztschr. anal. Chem.* **28**, 324.

The author prepares chromic chloride  $\text{Cr}_2\text{Cl}_6$  by passing chlorine over heated ferro-chrome in a glass combustion tube. He states that the separation from iron and manganese is very perfect, and that chromic chloride thus obtained is very pure. He uses a ferro-chrome containing about 21 per cent. of chromium. The tube must be large enough to afford free passage for the volatile ferric chloride. The chromic chloride thus prepared is insoluble in water and consists of long and very beautiful needles of a velvety, deep violet, shining appearance. In an experiment conducted in the same manner on ferro-tungsten, the author obtained a mixture of most beautiful needles of scarlet tungstic monoxy-chloride  $\text{WOCl}$ , and yellow tungstic dioxy-chloride  $\text{WO}_2\text{Cl}_2$ . As is well known, the former changes very quickly into the latter.

A. A. B.

**Oven for Heating Crucibles.**—H. von Jüptner, *Chem. Zeit.* **13**, 1303. This is made by cutting asbestos paper, as shown in

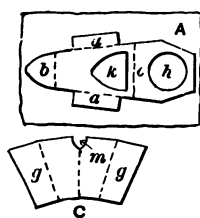
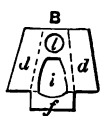


Fig. 1.



*A*, *B* and *C* (Fig. 1). *A* forms the bottom and ends of the oven by bending the parts *aa*, *b* and *c* upward at the dotted lines and cutting out the parts *h* and *k*.

*B* forms the support for the crucible with the parts *l* and *i* removed and *dd* bent downward. This part fits inside *aa*, *c* and *b* (Fig. 2). *C* forms the top with *gg* bent downward to fit between *aa* and *dd*. These parts are fastened together with wire bands, to give firmness to the oven.

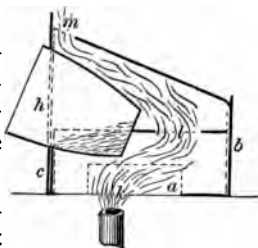


Fig. 2.

s. c.

**The Purification of Mercury.**—J. M. Crafts, *Bull. Soc. Chim.*, **49**, 856. The apparatus consists of a glass tube about 1.5 meters long and 5 centimeters in diameter, placed in a slightly inclined trough. The lower end is closed by a cork through which passes a funnel tube for pouring in the mercury and a tube with

a stop-cock for withdrawing it. The upper end is connected with an aspirator.

The process consists in drawing bubbles of air through the mercury for about forty-eight hours, by which means all of the base metals amalgamated with the mercury are oxidized and carried, together with any other impurities which may be present, to the upper end of the tube, forming a layer of dross. The purified mercury can then be drawn out by opening the stop-cock at the other end. Ordinarily only 24 hours are required to completely remove all impurities contained in the mercury, excepting, of course, gold and silver, which can only be removed by distillation. A tube of the size mentioned holds about 20 kilos of mercury, and, unless the metal is very impure, the tube can be used several times without cleaning.

The author shows that mercury is scarcely, if at all, oxidized by a current of pure air. The method therefore, commends itself as being convenient and satisfactory. The author also finds that mercuric oxide is totally insoluble in mercury. I. A. P.

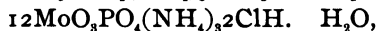
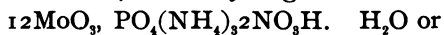
## INORGANIC ANALYSIS.

### **Analytical Studies on Phosphododekamolybdic Acid.—**

Dr. Franz Hundeshagen, Chem. News **60**, 168, 177, 188, 201, 215. (*Zeitschrift für analytische Chemie* **28**, 141.)

Dr. Hundeshagen has made an exhaustive study of the conditions of the formation of yellow phospho-molybdic acid and its separation as ammonium phospho-molybdate. The heads under which he discusses the subject are as follows:

1. *Influence of the Nature of the Solution upon the Composition of the Precipitate.*—Under the most varying conditions, the composition of the precipitate, dried at 130°–150°, after washing with cold dilute acid was found to be  $12\text{MoO}_3, \text{PO}_4(\text{NH}_4)_3$ . Dried in the desiccator over calcium chloride and caustic potash until the weight became constant, the analysis gave a formula of



depending upon the acid used in its precipitation and washing, but both acid and water was completely expelled at a temperature of about 130°.

2. *Influence of the Proportion of Ammonium Salt (Nitrate) in its Solution, upon the Separation of the Precipitate.*—From 5 to 10 per cent. of ammonium nitrate seemed to effect the most rapid separation.

3. *The Conditions of Temperature and Concentration.*—The precipitation is more rapidly made in a hot solution and the precipitate in this case is more crystalline and less likely to run through the filter paper than when made in the cold.

4. *Influence of the Degree of Acidity of the Solution upon the Formation of the Phosphododekamolybdate.*—Excess of acid prevents, as is well known, complete precipitation of phosphomolybdate.

(a.) *The formation of the Triammoniumphosphododekamolybdate from its elements present in Neutral Solution under the Influence of Nitric Acid.*—The conclusion is drawn from the experiments that the formation of the phosphododekamolybdate depends upon the presence of monammonium phosphomolybdate and dihydrophosphate, and on the condensation of two molecules of the former and one molecule of the latter, two molecules of water being eliminated, therefore the yellow phosphododekamolybdic acid should be a phosphodiexamolybdic acid.

(b.) *Influence of an Excess of Nitric Acid upon the formation and Dissociation of Phosphododekamolybdic Acid and the Quantity of Molybdic Acid Requisite for its Separation.*—The formation of ammonium phosphomolybdate is prevented when 1874 molecules of free nitric acid are present.

5. *Influence of the Proportion of Foreign Salts in the Solution, upon the Formation and Separation of Ammonium Phosphomolybdate.*—Experiments were conducted in the presence of ammonium sulphate and borax. For solutions containing very large amounts of sulphate, the ammonium phosphomolybdate could not be completely eliminated, but solutions containing borates, allowed a complete separation, after the boric acid was all liberated by nitric acid.

*Action of Salts, of Water, and Acids upon Preformed Ammonium Phosphomolybdate.*—The results of experiments under varying conditions are stated. The most suitable wash for ammonium

phosphomolybdate was found to be ammonium nitrate or chloride, both cold or warm (a 5 per cent. sol.) then follow acidulated solution of ammonium sulphate (5 to 10 per cent.) and dilute nitric or hydrochloric acid (1 to 2 per cent.) but these acids must not be left long in contact with the precipitate. Water at common temperature must be avoided, but for rapid washing, ice cold water may be used, and for neutral washings cold solutions (about 5 per cent.) of neutral ammonium nitrate or chloride.

*The Titration of Phosphoric Acid with Molybdic Acid, and that of Molybdic Acid with a Solution of Phosphoric Acid.*

Directions are given for titrations of solutions containing phosphoric acid with standard molybdic solution, and for titrating molybdic acid solutions by a solution of phosphate (sodium hydrophosphate.)

The article is concluded with some remarks on Finkener's method of direct weighing of the phospho-molybdate, which the author considers preferable to that of Hehner if the following directions are observed: The precipitate of phospho-molybdate is dissolved (after washing with a 5 per cent. solution of ammonium nitrate) in warm dilute ammonia, and if the precipitate is washed off the filter paper the solution must be filtered before evaporation, to remove any fibers of paper present. The filtrate is then put into the capsule and evaporated till only a faint odor of ammonia is perceptible, dilute nitric is then added, and the solution again evaporated. The thick residue is heated over a wire gauze, at first gently until the ammonium nitrate is all expelled, which may be determined by placing a watch glass over the crucible, and if after half a minute it is not coated all the nitrate is volatilized. The yellow pulverulent residue is triammonium phosphomolybdate, free from moisture and acid, which is weighed in a covered capsule after drying in the desiccator. The per cent. of  $P_2O_5$  in the precipitate is 3.794, (Finkener). Formula requires 3.78 per cent. The mean of a number of weighings is 3.753 per cent.

The author gives the following indirect methods:

(1.) *Saturation with Alkali.*—The precipitate, after being washed with a cold neutral solution (5 per cent.) of ammonium nitrate, is put into a beaker along with the filter and stirred with a glass rod. The volume of water must not be less than 30 cc. to

0.010 gms  $P_2O_5$ . A standard solution of soda lye is now run in, using phenolphthalein as an indicator until the liquid becomes red. When the precipitate is all dissolved, nitric acid is used to titrate back, until all color has disappeared. 23 molecules of NaOH are needed to neutralize the molecule of ammonium phospho-molybdate. 1 cc. of a decinormal solution soda-lye ( $=0.008$  gms. NaOH) $=0.016322$  gms. ammonium phospho-molybdate, 0.00061739 gms. phosphoric acid, and 0.015026 gms. molybdic acid.

(2.) *Precipitation from a Neutral Solution by Nitric Acid.*—The washed precipitate is dissolved in ammonia, then about ten per cent. of ammonium nitrate added, exactly neutralized and titrated with nitric acid until complete precipitation takes place, or the neutral solution is thrown down with an excess of standard nitric acid, filtered, washed and the excess of nitric acid determined in the filtrate. 1 cc.  $\frac{n}{10}$  nitric acid  $=0.0126$  gms.  $HNO_3 = 0.01444$  gms. ammonium phospho-molybdate, 0.00054616 gms. phosphoric acid and 0.0132923 gms. molybdic acid. A. H. W.

#### **Estimation of Silica and Analysis of Siliceous Materials.**

—George Craig, Chem. News **60**, 227. 20 or 25 grains of finely pulverized material are placed in a deep platinum crucible. A quantity of  $H_2SO_4$  more than sufficient to form sulphates with all the bases present is then added, and finally 50 grains of pure HF. After mixing well by shaking gently, the crucible is put over the lowest flame of an argand burner until almost dry. In order to ensure complete volatilization of the  $SiO_2$ , it is always best to renew this operation, heating more strongly at the close *until  $H_2SO_4$  is evolved*. This last point is very important in the determination, as by neglecting it, subsequent precipitation of fluorides will cause erroneous results. The test applied is to hold a glass rod moistened with dilute  $NH_4OH$  in the fumes, and then dip it into a test-tube containing dilute  $BaCl_2$ . When the crucible is cold, the contents are dissolved in HCl, the crucible being covered with a platinum capsule containing water, while heat is applied. After perfect solution, the acid contents are washed into a beaker. When separating the  $Al_2O_3$ , the solution is colored with litmus and  $NH_4OH$  added until the blue color just appears, and the red precipitate is filtered as soon as it settles, and washed



with water containing a little  $\text{NH}_4\text{NO}_3$  until free from  $\text{SO}_3$ , all the  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ , and a little  $\text{Mn}_2\text{O}_4$  are obtained in this precipitate, while the bulk of the manganese, practically all when but little is present, is precipitated by  $\text{NH}_4\text{OH}$  and bromine water, and  $\text{CaO}$  and  $\text{MgO}$  are determined in the filtrate. Alkali is estimated by Laurence Smith's process. Weighing as sulphate, estimating and deducting the  $\text{SO}_3$ , is the most rapid method of obtaining the amount of  $(\text{KNa})_2\text{O}$ . A. H. W.

**Water Analysis.**—Chem. News 60, 203. (From the Report of the Committee consisting of Professors Dewar, F. Frankland, Pery F. Frankland (secretary) Odling, and Mr. Crookes, appointed to confer with the Committee of the American Association for the Advancement of Science, with a view of forming a uniform system of recording the results of Water Analysis. Read before the British Association, Section B, Newcastle Meeting.) The committee report, that as regards the method of statement for general use in published analyses, they are of the opinion.

(1.) That it should be on the decimal system, preferably parts per million (mgms. per liter) or parts per 100,000, as parts per 1,000 (gms. per liter) would too frequently give rise to fractional results. They do not agree with the American Committee that different scales should be adopted for mineral and potable waters respectively, thinking that such a dual system would lead to confusion.

(2.) Great importance is attributed in every case to the clear statement of the actual analyses made, and results derived by calculation are to be strictly distinguished from those obtained by direct determination.

(3.) As regards the statement of the mineral ingredients, the suggested methods of the American Committee is approved, viz., recording the proportion of each metallic element (K, Na, Li, Ca, Mg, Fe,  $\text{Fe}_2$ , etc.) as well as that of each of the electro-negative elements (F, Cl, Br, I, S, etc.) contained in binary compounds, while in the case of oxy-compounds the electro-negative element as given as combined with the whole of the oxygen ( $\text{SO}_4$ ,  $\text{PO}_4$ ,  $\text{NO}_3$ ,  $\text{CO}_3$ , etc.), but the absence of any recognized name for these acid groups, as well as the common method of estimating the metallic

elements in the condition of bases ( $K_2O$ ,  $Na_2O$ ,  $CaO$ ) are considered objections to the system.

(4.) The amount of dissolved gases ( $O$ ,  $N$ ,  $CO_2$ ,  $H_2S$ , etc.) may be most conveniently expressed either in cubic centimeters, per liter, or in volumes of gas per 100 volumes of water, the latter being the practice generally in vogue in England.

The results of a complete analysis are to be tabulated as below, according to the committee's report :

*Results of Analyses expressed in Parts per 100,000.*

POTABLE WATER.

Total Solid Matters	{ (a) For suspension . . . . .
	{ (b) For solution . . . . .
Organic carbon . . . . .	
Organic nitrogen . . . . .	
Oxygen consumed, as indicated by decoloration of permanganate . . . . .	
Ammonia expelled on boiling with sodium carbonate . . . . .	
Ammonia expelled on boiling with alkaline permanganate . . . . .	
Nitrogen as nitrates and nitrites . . . . .	
Chlorine . . . . .	
Hardness	{ Temporary . . . . .
	{ Permanent . . . . .
	{ Total . . . . .

MINERAL WATER.

Carbonate of lime ( $CaCO_3$ ) . . . . .
Carbonate of magnesia ( $MgCO_3$ ) . . . . .
Carbonate of Soda ( $Na_2CO_3$ ) (Calculated from residual alkalinity after boiling and filtering off precipitated $CaCO_3$ and $MgCO_3$ ) . . . . .
Total Calcium ( $Ca$ ) . . . . .
Total Magnesium ( $Mg$ ) . . . . .
Total Potassium ( $K$ ) . . . . .
Total Sodium ( $Na$ ) . . . . .
Iron (ferrous) ( $Fe$ ) . . . . .
Iron (ferric) ( $Fe_2$ ) . . . . .
Sulphuric Radical ( $SO_4$ ) . . . . .
Nitric Radical ( $NO_3$ ) . . . . .
Nitrous Radical ( $NO_2$ ) . . . . .
Phosphoric Radical ( $PO_4$ ) . . . . .
Silicic Radical ( $SiO_3$ ) . . . . .
Chlorine ( $Cl$ ) . . . . .
Bromine ( $Br$ ) . . . . .
Iodine ( $I$ ) . . . . .
Sulphur as sulphide ( $S$ ) . . . . .

## DISSOLVED GASES.

Cubic centimeters of gas at 0°C. and 760 mm. in 1. L. of	
Water . . . . .	
Carbonic Anhydride (CO <sub>2</sub> ) . . . . .	
Oxygen (O) . . . . .	
Nitrogen (N) . . . . .	
Sulphuretted Hydrogen (H <sub>2</sub> S) . . . . .	

A. H. W.

**Rate of Decomposition of Chlorine Water by Light.**—

G. Gore, Chem. News **60**, 271. The author has carefully investigated, by means of the voltaic balance, the kind and amount of chemical change, the rate of decomposition, and the chemical composition of the products formed at all stages, when chlorine-water is decomposed under the action of daylight and sunlight. Two periods are recognized. During the first, there is a gradual but very great loss of voltaic energy, and hydrochloric, hypochlorous, and chloric acids are formed. During the second, a moderate and very slow increase of voltaic energy takes place, hypochlorous and chloric acids are decomposed, more hydrochloric acid is formed together with hydrogen peroxide, while under influence of prolonged sunlight, the whole of the oxygen of the hypochlorous and chloric acids unites with water to form peroxide of hydrogen, and this combines with the hydrochloric acid to form a definite "solution compound," having a formula of  $2\text{HClH}_2\text{O}_2$ . During the first period, forty consecutive measurements of the voltaic energy, at stated intervals, were made, showing a decrease from 1219 millions to 2.9 millions, while during the the second period, eight similar measurements were made, and the energy increased to 9.3 millions.

A. H. W.

**A Rapid Method of Detecting Tin in Minerals.**—Alexander Johnstone, Chem. News **60**, 271. After the reduction of the ore on charcoal with the ordinary fluxes by the use of the blowpipe, the ignited residue is cut out and removed to a mortar and the non-metallic particles are separated by washing with water. To prove that the metallic silvery scales remaining are tin, two or three drops of boiling concentrated hydrochloric acid are thrown over them in the mortar, and then one drop of a water solution, rather concentrated, of gold chloride is added from a glass tube. If tin is present, the characteristic "purple of Cassius" will appear on

the bottom of the mortar (porcelain or earthenware). As a confirmatory test, a current of sulphuretted hydrogen is directed against the moist, stained bottom of the mortar, forming brown stannous sulphide in the presence of the metal. A. H. W.

**Determination of Tungsten in Metallic Tungsten.**—Alfred Ziegler, Chem. News **60**, 272, (from "Chemiker Zeitung.") The author gives the following method for roasting of tungsten which only requires three-quarters of an hour.  $\frac{1}{2}$  gms. finely ground tungsten is thrown upon ammonium nitrate, (dehydrated) melting at a low temperature in a platinum crucible. Heat is applied until all the nitrate is driven off, leaving the partially oxidized metal in the crucible, which may now be completely oxidized without injury to the crucible, by means of a full Bunsen flame, stirring carefully with a stout platinum wire. The rest of the determination is executed in the usual manner. A. H. W.

**Preparation of a Standard Solution of Ferric Salts without Titration.**—William French, Chem. News **60**, 271.

A weighed quantity of ferrous ammonium sulphate, is dissolved in water, a little sulphuric acid is added and then a small quantity of hydrogen peroxide. The solution is then warmed and finally boiled to expel excess of oxygen and decompose traces of hydrogen peroxide. The whole operation takes about half an hour, and the solution need not be standardized. A. H. W.

**The Colorimetric Methods for the Determination of Nitrates in Potable Waters.**—Dr. Samuel Rideal, Chem. News **60**, 261.

The "phenol sulphuric" acid, and the "carbazol" methods were used comparatively with the following results.

<i>Nitrogen in Parts per 100,000.</i>		
Sample.	Phenol Sulphuric Acid.	Carbazol.
1 . . . . .	0.025	0.0247
2 . . . . .	0.050	0.045
3 . . . . .	0.200	0.209
4 . . . . .	1.400	1.380
5 . . . . .	1.600	1.650

For the "phenol sulphuric acid" method, are required standard solution of (a) potassium nitrate (0.7215 gms. to a liter of dis-

tilled water or 1 cc. = 0.0001 gms. nitrogen) and (b) phenol sulphuric acid, made by dissolving 15 gms. pure crystallized phenol in 92.5 cc. of sulphuric acid, free from nitrates, diluted with 7.5 cc. of water. Concentrated sulphuric acid and dilute ammonia solution are also needed. The details of the process are as follows:

A known volume of the water (100 or 25 cc. according to supposed richness in nitrates) is evaporated to dryness in a porcelain dish. 1 cc. of the phenol sulphuric acid is added to the dry residue, and then 1 cc. of distilled water and 3 cc. of concentrated sulphuric acid, and the mixture is gently warmed, when a distinct yellow color appears if nitrates are present in appreciable amount. The contents of the dish are now diluted to about 25 cc., and a slight excess of ammonia is added, and the solution is poured in into a narrow Nessler tube (14" × 1"), the dish is washed, and the washings added to the liquid in the tube. The whole is then diluted to the 100 cc. mark. The color of the solution is compared with that produced by repeating the operation with the standard potassium nitrate solution.

For the "carbazol" method, the standard potassium nitrate and concentrated sulphuric acid are also needed and in addition the following reagents: (a) silver sulphate solution, containing 4.3945 gms. per liter (1 cc. will precipitate 1 part chlorine per 100.000 from 100 cc. of water); (b) aluminum sulphate, free from chlorides and iron, 5 gms. per liter; (c) carbazol solution, 0.6 gms. carbazol is dissolved in glacial acetic acid and the solution made up to 100 cc. with the acid. 1 cc. of this solution is mixed with 15 cc. of sulphuric acid, for an analysis. A series of solutions, containing 0.03, 0.05, 0.07, etc. parts of nitrogen per 100.000, were also prepared from the standard nitrate solution by diluting with water (as recommended by the author of the carbazol method, S. C. Hooker). The method of washing is first to ascertain the amount of chlorides in 100 cc. of the water, next to add sufficient silver sulphate solution from a burette to precipitate all the chlorides. 2 cc. of aluminum sulphate is added to this solution and the whole made up to a convenient bulk, (110 cc. in waters containing 1 to 6 parts of chlorine per 100.000) and filtered. 2 cc. of the filtrate are used for the nitrate determination, by adding 4

cc. of sulphuric acid to it in a test-tube, well cooling the mixture, and then 1 cc. of carbazol solution in sulphuric acid as before described, when a bright green color will appear in a few minutes. The amount of nitrates is roughly estimated, then 2 cc. of the standard nitrate solution considered to be equal to it is placed in a second test-tube and compared with a fresh 2 cc. of the water. The author states that .0006 mgms. of nitrogen as nitrate may be detected by the carbazol method and Dr. Rideal obtained satisfactory results as shown before.

A. H. W.

**Separation of Zinc from Manganese.**—G. Neumann, *Ztschr. anal. Chem.* **28**, 57.

The author refers to the fact that while working on the separation of zinc as sulphide from other metals in a solution of formic acid, he saw the paper by Max. Brazard (*Ztschr. anal. Chem.* **27**, 209), treating almost exactly the same subject. The results arrived at were the same, and the author adds that his experience shows that the separation of zinc from iron and nickel by the formic acid method is very useful and the same method gives satisfactory results in the separation of zinc from manganese. The test analyses made on mixtures of different proportions of 1-10 normal solutions of zinc sulphate and potassic manganous sulphate give results a little too high in zinc, which the author attributes to the efflorescence of the zinc sulphate used, as he rarely found manganese in the zinc sulphide obtained.

A. A. B.

**Estimation of Alumina and Oxide of Iron in Phosphates.**—E. Glaser, *Ztschr. angew. Chem.* **89**, 636. The author recommends the separation of the lime as sulphate in an alcoholic solution before the precipitation of the iron and alumina as phosphate. The results given in the paper are very good, both in artificially prepared samples and in guanos.

J. E. W.

**A New Process for the Volumetric Estimation of Bromine in Presence of Chlorine and Iodine.**—Norman McCullough, *Chem. News* **60**, 259. A decinormal solution of potassium permanganate is prepared by dissolving 31.9 grams of the salt in 10,000 gms. of water. The solution is then standardized as follows: A known weight (from 3 to 5 grains) of pure dry iodine is dissolved in a little sodium hydroxide in a glass-stoppered bottle

of about 5 ozs. capacity, and  $\frac{1}{2}$  oz. or so of strong hydrochloric acid is added, the stopper replaced and the contents cooled. Potassium permanganate is now run in, chloroform is added as an indicator, and the solution is well shaken after each addition until the free iodine is all converted into the colorless monochloride, by the chlorine liberated by the reaction between the hydrochloric acid and the permanganate. The iodine equivalent of the permanganate is calculated to bromine by multiplying by the factor 0.6713, and each division (10 grains) equals about 0.04 grains bromine considered as the hydracid. A semi-normal standard solution of potassium iodide (82.78 grains KI in 10.000 grains  $H_2O$ ) is also standardized with the permanganate by the foregoing process for iodine and should be equivalent to the permanganate, bulk for bulk. Chloroform, a three per cent. solution of hydrocyanic acid and a strong solution of manganous chloride are also needed. The chloroform is well shaken with a few divisions of permanganate and enough hydrochloric acid to decompose this, to free it from any oxidizing or reducing impurity. Potassium iodide is then added to liberate free iodine, and the color imparted to the chloroform discharged by sufficient permanganate, when the chloroform is washed free from acid liquor. The hydrocyanic acid solution is made by decomposing 600 grains of KCN (95 per cent.) dissolved in  $13\frac{1}{2}$  ozs. of water, and kept well cooled by a freezing mixture of ammonium chloride and potassium nitrate, with  $2\frac{1}{2}$  ozs. of hydrochloric acid, diluted with an equal bulk of water. The cool solution is now titrated with permanganate to destroy oxidizable impurity until permanently pink in color.

The manganous chloride solution is prepared by dissolving one-half pound of the crystallized salt ( $MnCl_2 + 4H_2O$ ) in 4 ozs. of warm water and cooled and contains 58 per cent. of  $MnCl_2$ . The use of this solution is to prevent the injurious action of free hydrochloric acid, and a solution containing one-third its volume of hydrochloric acid is amply provided with the manganous chloride if it contains three molecules to four of hydrochloric acid. For the practical investigation of this method a standard bromide was used, made by distilling excess of bromine in presence of potassium bromide into a pure caustic soda solution, evaporating to dryness and calcining at a red heat. The estimations were

conducted in a glass stoppered bottle. The weighed bromine was dissolved in a quantity of water, (not more than half an ounce) and one ounce of manganese solution was then added. Standard permanganate was then added in excess of from 10 to 30 divisions of the theoretical amount, when the bottle was plunged into the freezing mixture referred to before until the temperature was not above 55° F. The bottle was then removed, hydrochloric acid added to dissolve the manganic hydroxide, and from 30 to 60 grains hydrocyanic acid were then poured in and the bottle replaced in the cooling solution until complete reduction had taken place. Half an hour was sufficient with the excess of permanganate used above, and the solution was then titrated with the potassium iodide, until nearly decolorized from the complete decomposition of the manganic chloride, and then slightly recolored from liberation of free iodine, indicating excess of the iodide, which excess was afterwards accurately determined by adding a little chloroform and titrating with potassium permanganate. The results tabulated speak for the accuracy of the above method.

A. H. W.

**Ammonia Free Water.**—A. G. Bloxam, *Chem News* 61, 29. A simple method of obtaining ammonia free water is given, which consists in boiling ordinary distilled water in a wide-necked flask. Half a gallon of water free from ammonia, it is stated, may be thus obtained in less than an hour.

A. H. W.

**On Schützenberger's Process for the Estimation of Dissolved Oxygen in Water.**—Henry E. Roscoe and Joseph Lunt, *Journ. Chem. Soc.* 1889, 552-576. The process has been thoroughly examined and many errors found in the manner in which it is usually employed, and correction for the same proposed. The work is done in a most careful and painstaking manner, the report of which extends over twenty-four pages. It was found that the results obtained were not concordant with the same water; that high results were obtained when the titration was performed quickly; that the results were low when the water had been exposed to hydrogen and that this loss was due to diffusion. The diffusion depends upon the size and shape of the vessel holding the water; the volume of hydrogen; the time of exposure and



the volume of water. The apparatus and the method of using is described by the authors as follows :

“(1.) An apparatus for the continuous generation and purification of hydrogen by the action of dilute sulphuric acid on zinc;

(2.) A 200 cc. wide-mouthed bottle fitted with three burettes with glass tops, inlet and outlet tubes for a current of hydrogen, and an outlet tube for the titrated liquid ;

(3.) Winchester stock-bottles of hyposulphite, indigo and water, communicating with their respective burettes by glass syphons.

A sample of water is examined by the new method as follows :

(1.) 20 cc. of the water is introduced into the small bottle and about 3 cc of indigo solution added.

(2.) A moderate current of hydrogen is passed through the blue liquid by a very fine jet for three minutes to free both water and supernatant gas from free oxygen.

(3.) Hyposulphite is now carefully added, during the flow of hydrogen, until the change from blue to yellow occurs, taking care not to overstep this point.

(4.) A further measured quantity of hyposulphite is now added (10 cc.), sufficient to combine with all the dissolved oxygen in the volume of water, 50–100 cc., proposed to be used in the estimation.

(5.) The important point now is, that the water is run in from a burette by a capillary tube passing beneath the surface of the liquid to the bottom of the vessel. Thus we introduce the water into a liquid which will at once combine the free oxygen and thus prevent its diffusion on coming in contact with the hydrogen, the reduced indigo acting as an indicator for the complete oxidation of the hyposulphite. The liquid is kept in constant motion during the addition of the water, which is shut off the moment a permanent blue color appears.

(6.) The blue is decolorized by a further slight addition of hyposulphite. The volume of water used, and the total hyposulphite, minus the first addition, are noted and the estimation repeated for confirmation.

As the oxygen value of distilled water saturated with air must be known to standardize the hyposulphite solution, an apparatus was devised by means of which the water could be boiled in vacuo and the gases subsequently measured after having been transferred to a gas apparatus.

The following table of mean values was obtained :

*Dissolved Gases in Fully Aerated Distilled Water at 760 mm. (dry).*

Temperature.	N.	O.	Total Gas.	Percentage of Oxygen.
10° C.	15.47	7.87	23.34	33.74
15° C.	13.83	7.09	20.92	33.86
20° C.	12.76	6.44	19.20	33.55
25° C.	11.78	5.91	17.69	33.40

The modified volumetric method was compared with the results obtained by boiling the water in vacuo. Quite concordant results were obtained. If the water contains small quantities of either free acid or alkali the results are not accurate. All connections in the apparatus used must be made as far as possible without rubber tubing as the air diffuses quite freely through it.

C. W. M.

**On a Volumetric Method of General Applicability for the Determination of Combined Sulphuric Acid.**—Launcelot W. Andrews, Amer. Chem. Journ. 1889, 567. This method may be used in the presence of magnesium, calcium, aluminum, zinc, manganese, iron (ferric), nickel, cobalt and silver. A solution of barium chromate, 2–4 per cent., in hydrochloric acid is made by heating barium chromate with water containing 36 gms. of hydrochloric acid per liter.

To a boiling dilute solution of the sulphate an excess of the barium chromate solution is added and the boiling continued a minute or more. Pure calcium carbonate is then added until an addition no longer causes an evolution of carbonic acid. The solution is again boiled and filtered hot and the precipitate washed with hot water. After the filtrate has cooled crystals of potassium iodide and a few cc. of hydrochloric acid are added and the amount of iodine set free titrated with sodium thiosulphate and this calculated to  $\text{SO}_4$ . The results are very accurate compared with gravimetric determinations. In case the solution contains iron, nickel or zinc,

ammonium hydrate is to be used in the place of calcium carbonate, and the excess boiled off before filtering. C. W. M.

**On the Occurrence of Arsenic in Bone-Meal and Methods for its Determination.**—H. Fresenius, *Ztschr. anal. Chem.* **28**, 64.

Bone-meal or precipitated phosphate of lime is now very generally fed in small amounts to cattle. It is made by treating bone ash or steamed bones with hydrochloric acid and neutralizing the solution with lime water. The finely divided precipitate of phosphate of lime is washed in a filtering press and dried, when it is ready for market. If the hydrochloric acid used contains arsenic, as is usually the case with the commercial acid, arsenite or arsenate of lime will be precipitated with the phosphate. The effect of the arsenic in bone meal upon the condition of the cattle to which it is fed has not been carefully studied, but the fact of its presence has caused some inquiries and many samples have been sent to the Agricultural Experiment stations to be examined for arsenic. The author discusses several methods for the quantitative determination of arsenic in bone meal.

1. Solution in hydrochloric acid, precipitation by sulphuretted hydrogen and weighing of the sulphide of arsenic. This method, he says, gives too high results on account of the presence of organic matter, which precipitates with the sulphide of arsenic.

2. Fusion with carbonate of soda and nitre, solution in water, filtration and determination of the arsenic in filtrate as the ammonia magnesian arsenate or as sulphide of arsenic.

3. Distillation with hydrochloric acid, and ferric chloride and determination of the distillate as arsenic tri-sulphide by precipitation with sulphuretted hydrogen.

The last method he considers the best and recommends the apparatus described in the paper by R. Fresenius and E. Hintz (*Ztschr. anal. Chem.* **27**, 179), proceeding as follows: Weigh into the retort 10 gms. of the substance and 100 cc. strong hydrochloric acid, 1.19 sp. gr. When solution is nearly complete add 5 cc. of a cold saturated aqueous solution of ferrous chloride, and distil until only a small amount of the liquid remains in the retort. In this way one distillation is sufficient to transfer all the arsenic to the receiver as trichloride, for the addition of more hydrochloric

acid and ferrous chloride to the mass in the retort failed to show after another distillation even a trace of arsenic in the distillate; nor could any be detected by fusing the residue in the retort with caustic potash and nitre and testing the aqueous filtrate from the fusion. Precipitate the arsenic in the distillate by sulphuretted hydrogen, filter and weigh, with the proper precautions as arsenic tri-sulphide. After weighing treat the precipitate with ammonia and carbonate of ammonium; it should dissolve completely without leaving any residue of organic matter. Should there be any residue the arsenic may be reprecipitated by acidulating the alkaline filtrate with hydrochloric acid and passing sulphuretted hydrogen into it again. This purified precipitate may be filtered and weighed.

The amounts found in bone-meal vary from 0.028% to 0.170% of metallic arsenic. The author regrets that no experiments have been made to test the effect of doses of bone-meal containing increasing amounts of arsenic on animals; the experiments described by Weiske (*Jour. f. Landwirtschaft*, **23**, 317) of finding arsenic acid not giving, in his opinion, sufficient data to fix a maximum for the amount of arsenic to be allowed in bone-meal.

A. A. B.

#### **Determination of Tungsten in Rich Tungsten Alloys.—**

Dr. Jos. Preusser, *Ztschr. anal. Chem.* **28**, 173.

To avoid the tedious method of oxidizing the powdered alloys with aqua regia, an operation which the author states frequently requires 5 to 6 days, he suggests a preliminary roasting of the finely divided sample. The method is as follows: Weigh from 0.5 to 1 gm. of the sample powdered in a steel mortar and bolted through linen, into a flat porcelain dish and heat it over a Bunsen burner or in a muffle until the color of the powder changes from the greenish yellow of the partly oxidized tungstic oxide to the pure yellow of tungstic acid. This will require only a few hours, but careful tests have shown that no loss of tungstic acid through prolonged or excessive heating may be feared. Transfer the mass to a porcelain dish and test it once with aqua regia to insure complete oxidation of the tungstic oxide; evaporate to dryness twice with hydrochloric acid and heat finally to 120° C. Treat with dilute hydrochloric acid, allow to stand for some hours and filter. Ignite the mass on the filter, consisting of tungstic and

silicic acid, in a platinum crucible and fuse it with 3 or 4 times its weight of sodic carbonate for half an hour over a blast lamp. Treat the cold mass with hot water and filter. Acidulate the filtrate, containing the tungsten as sodic tungstate, with hydrochloric acid, evaporate to dryness, redissolve in water, allow to stand for several hours, filter on the pump and wash with a dilute solution of ammonic nitrate. Place the filter containing the precipitate in an Erlenmeyer flask, dissolve any of the hydrate that may remain adhering to the porcelain dish in ammonia. Transfer it to the flask, add an excess of ammonia and digest it at a gentle heat on the iron plate. The tungstic acid dissolves as ammonic tungstate while the silicic acid remains insoluble. Filter, evaporate the filtrate to dryness in a weighed porcelain crucible, and ignite until the weight is constant and only the pure, straw colored tungstic acid remains.

A. A. B.

**The Separation of Barium, Strontium and Calcium.**—Prof. Kupferschlaeger, Bull. Soc. Chim. **49**, 854. A mixture of the three carbonates is treated with very dilute nitric acid, the carbonates being in slight excess, and the solution evaporated to dryness. The mass remaining is then taken up with water and the solution filtered and evaporated to complete dryness. The dried and perfectly neutral nitrates thus obtained are then treated to four successive additions of etherized absolute alcohol, the proportion of ether to alcohol being increased with each addition until equal parts of each are used. The treatment is effected in a small, well corked matarass and the solutions are filtered after standing long enough only to become clear. When the last addition of the etherized alcohol leaves no residue on spontaneous evaporation, the calcium nitrate is completely dissolved out. The nitrates of barium and strontium remaining are dissolved in water, the solution placed in a small test tube, and the concentrated solution of potassium bichromate added, little by little, until there is no further precipitation. The precipitate is washed with water containing alcohol and heated with sulphuric acid, to convert the calcium chromate into sulphate. To the filtrate containing the strontium, diluted sulphuric acid is added and the solution heated moderately, by which all the strontium is precipitated as sulphate.

By this method the quantity of the reagents used and the num-

ber and length of the operation are reduced to a minimum, whilst each element is obtained in such a form as to be easily examined further for any traces of the other two which may remain.

I. A. P.

**The Determination of Nitrogen.**—P. Cazeneuve and L. Hugounenq, *Bull. Soc. Chim.*, **49**, 900. The authors have made an improvement upon Duprè's modification of the method of Dumas and claim that it is now superior to any other known. The carbon dioxide for the expulsion of the air is generated in the combustion tube itself by a layer of manganese carbonate along about 15 centimeters of the farther end of the tube. Manganese carbonate is found to be best for this purpose on account of its dryness, change of color during decomposition, and the fact that it does not re-absorb carbon dioxide on cooling. The remaining part of the tube is charged in the ordinary way. It is then put in communication with an aspirator by means of a small curved tube and a mercurial manometer. The air is now expelled from the tube by heating the manganese carbonate three times in succession, until the mercurial column of the manometer has completely descended. Without stopping the generation of the carbon dioxide, the combustion tube is placed in connection with the Duprè receiver, when the carbon dioxide collected will be found to be pure. The combustion is then proceeded with as usual. To avoid calculation, the volume of gas in the receiver is compared with a standard tube containing a known amount of nitrogen.

I. A. P.

**The Estimation of Dissolved Carbonic Acid.**—Leo. Vignon, *Bull. Soc. Chim.*, **49**, 903. This method depends upon the principle that free carbonic acid in aqueous solution can be titrated by standard lime water, using a saturated alcoholic solution of phenol-phthaleïn as indicator. For this purpose 50 cc. of the water to be examined are placed in a test glass supplied with a glass stopper and 10 drops of the phenol-phthaleïn solution added. The standard lime solution is then run in from a burette until a slight rose tint is visible. To render the determination more exact a second test glass containing the same amount of water, from which the carbonic acid has been expelled by boiling, is placed alongside of the first one and 10 drops of the phenol-phthaleïn

added. The liquid in the second glass is then slightly colored by a little of the lime solution, and the amount required to do this subtracted from the amount required to bring the water in the first glass to the same tint. This gives the exact amount of lime water necessary for the neutralization of the carbonic acid present. Towards the close of the operation the combination of the lime with the carbonic acid is rather slow, and the liquid must be stirred and the lime solution added drop by drop. The chlorides, sulphates and nitrates of lime and magnesia do not interfere with the reaction, nor does carbonate of lime. If the solution contains carbonate of magnesia, or alkaline salts of which the acids form insoluble salts with lime, a little neutral calcium chloride solution must be added to convert them into chlorides.

This method permits of the estimation of one part of carbonic acid in 469,000 parts of water.

I. A. P.

**On Water Analysis.**—H. M. Vernon, *Chem. News* **60**, 249. Since in evaporating water for estimation of organic carbon and nitrogen by Frankland's process, there is danger of decomposition of organic nitrogenous impurities, the author suggests that if the evaporation be carried on under a low pressure over strong sulphuric acid, the sources of error may be reduced to a minimum, but he has not experimentally tested his scheme.

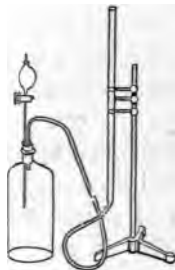
A. H. W.

**Determination of Oxygen in Water by Müller's Method.**—R. Hefelmann and K. Barth (*Chem. Zeit.* **13**, 1337) find this method to be inaccurate when much organic matter is present. The detection of nitrites with iodine solution is impossible in the presence of a larger amount of organic matter, and can be done only when the water has been acidified with sulphuric acid, a portion of it distilled with caustic soda, and the distillate acidified with acetic acid or dilute sulphuric acid. Small quantities of nitrites in the presence of much organic matter give the test with iodine solution for a minute or two and then it disappears. The free iodine is absorbed by the organic matter. Free chlorine is also absorbed in a similar manner.

S. C.

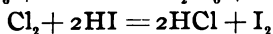
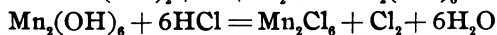
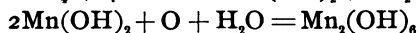
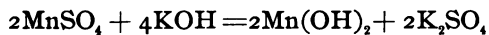
**Determination of Oxygen in Water.**—Max Müller, *Chem. Zeit.* **13**, 1188. The author finds, after a number of experiments, that in good water the amount of dissolved oxygen remains about

the same, while in contaminated water the oxygen disappears after standing a few days. He proposes to take advantage of this in making water analyses. The apparatus used is shown in the following cut.



The bottle or flask having a capacity of 2-3 liters is filled to the brim with the water to be analysed and 1 gm. manganese sulphate is added. The other part of the apparatus is connected with the long glass tube, and the latter is filled with the water to be analysed, so that the rubber tube is full to the cork. The cork is then placed in the neck of the bottle and the column of air in the funnel tube is removed by opening the stop-cock and raising the long glass tube so that the water rises just above the stop-cock. After closing the cock, 5 cc. of strong caustic potash or soda solution is poured into the funnel and allowed to run into the water. This forms a precipitate of manganous hydroxide which absorbs the oxygen in the water. At the end of half an hour, during which time the bottle is shaken frequently, the oxygen is all absorbed and the funnel tube is washed out with a little water, and a few crystals of potassium iodide dissolved in 15 cc. concentrated hydrochloric acid are allowed to run into the bottle. This dissolves up the hydroxides of manganese and liberates iodine. A measured amount of the water is taken and titrated with sodium thiosulphate solution to determine the amount of free iodine from which the amount of oxygen is calculated. The chief precaution is that no air be allowed to enter the bottle while running in the reagents.

The reactions which take place are these.



If the water contains nitrates the same amount as taken above must be treated with hydrochloric acid and potassium iodide and the free iodine determined. This result subtracted from the one previously obtained will give the amount of oxygen. The second



result may also be used to determine the amount of nitrates present in the water. S. C.

**Determination of Cadmium in Cadmium Dust.**—W. Minor, Chem. Zeit. 13, 1376. The author finds that a single precipitation of cadmium with sulphuretted hydrogen is not sufficient, and the results obtained are from 1–3% too high. He recommends the following method: 20 gms. cadmium dust are dissolved in hydrochloric acid and the excess of acid removed by evaporation. The filtered solution is then diluted to one liter and 50 cc. taken for analysis. The cadmium is precipitated with sulphuretted hydrogen, filtered through a weighed filter, washed with hot water, dried at 110°, and again weighed. This operation is repeated until the weight is constant. For every 0.4 gm. CdO 10 gms. hydrochloric acid (sp. gr. 1.19) should be used and this diluted to 250 cc.; washing the precipitated sulphide with alcohol and water containing sulphuretted hydrogen is unnecessary. S. C.

**A Sensitive Test for Certain Impurities in Mercury.**—Chem. News 61, 40. In investigating the “voltaic energy” method, which is used, Dr. Gore proceeded as follows: Two portions of very pure mercury in an electrolyte were connected with an astatic torsion galvanometer of 100 ohms resistance by means of insulated platinum wires. A sufficient amount of a very dilute amalgam of known strength, of a particular metal with some of the same mercury, was now added to one of the portions of mercury, so as to cause the needles of the galvanometer to be just visibly deflected while being viewed with a magnifying glass. 120 cc. of water were employed in each electrolyte, and the results of the investigation are tabulated below:

One Part of	1.0 grain of HCl or H <sub>2</sub> SO <sub>4</sub> in 120 cc. of water.	10 grains of KCl in 120 cc. of water.
	Parts of Mercury.	Parts of Mercury.
Mg . . . . .	110,274,000,000	13,430,858,806
Zn . . . . .	104,950,000,000	18,034,482,758
Cd . . . . .	184,828,432	10,404,225
Sn . . . . .	38,900,000	8,831,632
Cu . . . . .	15,484,375	1,640,160
Bi . . . . .	9,762,300	1,621,000
Pb . . . . .	5,651,149	1,050,341
Ag . . . . .	905	79

To find the minimum degree of electro-motive force required to visibly move the needles, one end of a single thermo-electric couple of iron and pure copper were heated  $9.6^{\circ}$  centigrade higher than the other end, or of one of platinum and copper  $49.5^{\circ}$  C. higher than the other, the opposite ends being immersed in vessels of oil, the result being 0.00013258 volt, or, approximately, this was the degree of electric-motive force of amalgam of 1 part of zinc dissolved in about 105,000 million parts of mercury, or of 1 part of magnesium with about 110,000 million parts of mercury, when opposed to pure mercury in solution at atmospheric temperature of sulphuric or hydrochloric acid of degree of strength given. As such minute portions of all the metals given in the list except silver may be thus detected, the method is applicable for testing the purity of mercury.

A. H. W.

**On the Precipitation of Alumina and Iron Oxide by Ammonia.**—G. Lunge, *Ztschr. angew. Chem.* 1889, 634.

Experiments were made on samples of a good quality of commercial sulphate of aluminum by dissolving in hydrochloric acid, adding ammonia in not too great excess, and boiling. A large platinum dish being used to obviate any bad results from the use of glass or porcelain. Experiments (a), (b) and (c) were precipitated with a decided excess of ammonia previously freed from any carbonic acid it might contain, in (d) the boiling was continued for about  $\frac{1}{2}$  hour, or until all free ammonia was expelled. (a) and (b) were ignited with the blast lamp, (c) with Muencke's burner, (d) first with the burner and afterwards with the blast. The results differ but slightly.

$\text{Al}_2\text{O}_3$ , (after deducting  $\text{Fe}_2\text{O}_3$ )

(a) 15.77%, (b) 15.86%, (c) 15.88%, (d) 15.87%.

The author concluded that it is hardly possible to dissolve the precipitate by moderately long boiling, that the washing of the precipitate takes but little time, and that long heating of the precipitate is not necessary when it contains no sulphuric acid.

J. E. W.

**To Detect the Presence of Small Amounts of Nitrous Acid.**—G. Lunge, *Ztschr. angew. Chem.* 1889, 666.

The author used two solutions. First .5 gms. sulphanilic acid

dissolved in 150 cc. of acetic acid. Second, 1 gm. naphthylamine boiled in 20 cc. water. The residue separated by decantation and 150 cc. acetic acid added.

To make the test he uses 20 cc. of the solution to be examined, adds 1 cc. of the sulphanilic acid solution and heats to 70°–80°, then adds the naphthylamine solution. If the solution contains the smallest trace of nitrous acid a red color will appear in a minute or two.

J. E. W.

**On the Determination of Chlorine in Water.**—Allen Hazen, *Amer. Chem. Journ.* 1889, 11, 409.

In this paper is shown that the results obtained in titrating a solution containing a chloride by means of silver nitrate solution, using potassium chromate as an indicator, depend for their accuracy upon the amount of solution taken and the amount of indicator used. The author describes several experiments made, showing that on a certain volume of water operated upon, the results obtained increased with the amount of potassium chromate used; also that higher results were obtained on waters containing the same amount of chlorine when the volume of the water was increased. Directions are given for method of analysis. C. W. M.

**Determination of Iron in Water.**—J. C. Bell, *J. Soc. Chem. Ind.*, 8, 175.

Evaporate 70 cc. of the water to dryness and ignite the residue gently to burn off organic matter. Add 1 cc. of pure nitric acid and allow to flow over all the residue. Then evaporate off the nitric acid on the water-bath and again moisten residue with 1 cc. of a 10 per cent. solution of hydrochloric acid. To this add 5 or 10 cc. of distilled water, warm on a water-bath, and filter the solution into a 50 cc. Nessler tube. Add water to make filtrate 50 cc. and pour into a tube containing 1 cc. of freshly made ferrocyanide solution. To this mixture add 1 cc. of dilute nitric acid and compare with a tube containing a known weight of iron.

Standard solution of iron, 1 cc = .001 of iron. This is made by taking the purest and finest iron wire, dissolving in nitrohydrochloric acid, evaporating to dryness and taking up with a slightly acid solution of hydrochloric acid.

Standard ferrocyanide: 1 part of salt in 25 parts of water.  
Standard nitric acid: 50 cc. of strong acid made up to a liter.  
Standard hydrochloric: 100 cc. of strong acid made up to a liter.

It is absolutely necessary that a blank experiment be made with pure distilled water; if a slight blue color is obtained, a correction can be made in estimating the iron in the sample of water.

O. O. I.

**Determination of Sulphur in Coal.**—G. H. Bailey, J. Soc. Chem. Ind., 8, 360.

The author fuses the coal with magnesia and sodium carbonate, as in Eschka's method, oxidizes, by means of bromine water, and precipitates with barium chloride.

O. O. I.

**Determinations of Phosphorus in Phosphor-Tin.**—W. Hempel, Ber. 22, 2478.

On account of the insoluble compound which phosphoric acid forms with the stannic oxide, the analysis of phosphide of tin is particularly difficult.

The ordinary way of analyzing phosphide of tin by dissolving it in aqua regia and precipitating with sulphuretted hydrogen is not satisfactory, as a considerable quantity of phosphorus is thrown down with the precipitated sulphide as a basic phosphate of tin.

It is easily analyzed according to Wöher's method, by treating with chlorine, the chlorides of tin and phosphorus formed being collected in about 10 cc. of concentrated nitric acid. If the apparatus is rinsed with a solution of 1 part concentrated nitric acid and 2 parts of water, no trace of stannic oxide is precipitated.

The phosphoric acid is now easily precipitated in the usual way by molybdic acid.

If dilute nitric acid is taken a part of the phosphorus separates with the stannic oxide and the result will be too low.

O. O. I.

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## IRON AND STEEL.

**The Gotz Method for Determining Phosphorus in Steel.**—K. Borman, Ztschr. angew. Chem., 1889, 638.

1.2 gm. of steel is dissolved in a beaker of 100–125 cc. capacity by 25 cc. of nitric acid (900 cc.  $\text{HNO}_3$  1.4 sp. gr. + 100 cc.  $\text{H}_2\text{O}$ ), concentrated as much as possible and oxidized by 8 drops for ingot steel, or 16 drops for tire or spring steel, of permanganate of potash. The precipitate of manganese oxide formed is taken



up with 5 or 10 drops of hydrochloric acid 1.19, the excess of hydrochloric acid, driven off, and the solution again concentrated. To this hot solution, add 10 cc. of 25 per cent. nitrate of ammonia solution, then 25 cc. of Finkener's molybdate of ammonia solution, and rinse the contents of the beaker into the shaking flask with the ammonia nitrate solution. Fill the graduated tube, which is to receive the precipitate, to the mouth with the 25 cc. solution of ammonium nitrate solution, and notice that no air bubbles are in the column of liquid. Fill the shaking glass with ammonia nitrate solution, and fix it in the agitator.

The shaking flask, prepared by the author, is shown in the figure. It has a capacity of 60–70 cc. The tube is graduated to .02 cc. for 40 cc., and is 40 mm. in length. It is claimed that 30 minutes are sufficient for a determination of phosphorus, and that in 5 or 6 hours 60 or 80 determinations may easily be made.

J. E. W.

### **The Influence of Silicon on the Properties of Steel.—** Chem. News 60, 273, 289, 299.

The committee of the British Association, consisting of Professors Tilden and W. Chandler Roberts Austen and Mr. T. Towner (Secretary), appointed to investigate the influence of silicon on the properties of steel, have made some interesting discoveries, which are related in their Third Report. Mr. R. A. Hadfield investigated the alloys of iron and silicon, which are usually described as ferro-silicon and silicon spiegel, the latter containing manganese in addition. Mr. Edward Riley in 1872 was the first to undertake experiments with ferro-silicons. While the highest ferro-silicon yet obtainable contains only from 18 to 20 per cent. of silicon, a comparatively small amount, for rich ferro-manganese may contain 80 per cent. of manganese, yet the 20 per cent. ferro-silicon is better adapted for experimental work

than a 20 per cent, ferro-manganese, from the curious fact that as the silicon increases, the carbon decreases, the amount of carbon in an alloy of iron and silicon, containing 10 per cent. of the latter element, being not more than from  $\frac{3}{4}$  to 1 per cent., and most of this amount occurs as graphite. Mr. Keep, of Detroit, Mich., and Mr. Turner both find that white carbonaceous cast-iron, which would invariably give porous and brittle castings, are made free from honey combs and possess greater strength if small amounts of silicon are added. If further additions are made, up to 2 per cent., the iron becomes grey, and reaches its maximum strength. Silicon irons have the reputation of imparting fluidity to other brands, but this is due to the fact that the silicon has the property of changing the carbon from the combined to the graphitic form, and thereby causes a more fluid cast-iron. The popular belief that silicon should be absent or present in very small quantities in steel which has to be used in its forged state is correct as regards alloys of carbon, silicon, and iron, but it has now been demonstrated that silicon alloyed with iron, provided carbon is absent or only present in small quantities, gives good tests as to toughness and malleability. A fact, pointed out by Mr. Howe in his "Metallurgy of Steel, is that "silica is often mistaken for silicon; who knows how far that is responsible for this metalloid's bad name?" Silicon steel pipes or settles to a greater extent than ordinary steel, a disadvantage, and its fluidity is less than that of ordinary steel. The crystallization of the lower percentages is somewhat like ordinary steel, but on exceeding  $2\frac{1}{2}$  per cent silicon the crystals become very large, glazed in appearance, and on further additions, the material approaches to the appearance of silicon pig-iron and is non-malleable. High percentages of silicon in the cast or unforged material causes a considerable increase in contraction, a difficult problem for the steel founder. It is difficult to dissolve ferro-silicon drillings, and recourse is usually made to the sodium carbonate process, but silicon steel readily dissolves in hydrochloric acid and the silica residue is very clean and free from iron. The silicon is very uniform in this steel and the carbon is always present in the combined form.

A. H. W.

## ORGANIC ANALYSIS.

### **Note on the Purification of Alcohol for Laboratory Uses.**

—E. Waller, Jour. Am. Chem. Soc. 11, 124.

The alcohol to be purified is shaken with potassium permanganate until it assumes a decided color. It is then allowed to stand until the permanganate has been decomposed and brown manganese oxide is deposited. A little calcium carbonate is then added, and the alcohol distilled from a flask provided with a Wurtz, or LeBel-Heninger tube. 10 cc. of the distillate is tested from time to time with 1 cc. of strong caustic soda or potash solution, and when boiled should not have a yellow color on standing a short time. If the alkali does not impart a perceptible color to the alcohol the distillate may be preserved for use.

F. R. B.

### **Contributions to the Determination of Phosphoric Acid in Sweet Wines and Notes on their Critical Examination.—**

W. Fresenius, Ztschr. anal. Chem. 28, 67.

The author found in a recent analysis of Tokay wine that the phosphoric acid determined in the ash was below the limit proposed by List (Bericht über der 5. Versammlung der freien Vereinigung bayrischer Vertreter der angew. Chem. pag. 51, resp. 56.) While the proportion of extract to sugar was quite normal. He thought that as the sugar was very high, 31.92 gms. to 100 cc. wine, that some phosphoric acid might have been lost by the combustion of so much organic matter. To test the matter he determined the phosphoric acid in the samples in the different ways described below and found as follows:

- |  | gms. of $P_2O_5$ in 100 cc. wine. |
|--|-----------------------------------|
| 1. Direct determination in ash . . . . .   | 0.0336 and 0.0368                 |
| 2. Sugar partially removed by fermentation (after destroying alcohol) with yeast then evaporated down, the extract burned and $P_2O_5$ determined in ash . . . . .             | 0.0399 and 0.0412                 |
| 3. Sugar partially removed by fermentation using a very small amount of yeast . . .  | 0.0431                            |
| 4. The wine (50 cc.) was evaporated down with 6 gms. $Na_2CO_3$ , the dried mass thrown into melted $KNO_3$ , and the phosphoric acid was determined in the aqueous solution . | 0.0427                            |

(In 2 and 3 the amount of  $P_2O_5$  due to the yeast was subtracted).

In a Malaga wine containing only 13.76% sugar, the phosphoric

acid attained by the different methods scarcely varied. These results show that in very sweet wines it is necessary to remove the excess of sugar either by fusion with carbonate of soda and nitre, or by fermentation with a small amount of yeast. The former is the quicker method, and, although disagreeable, is to be preferred if time is lacking.

The author observes that according to the rules of normal composition proposed by List, a concentrated sweet wine, whether prepared from dry grapes or by the evaporation of grape juice, containing 20% sugar should give at least 4% extract free from sugar, and 0.04% phosphoric acid. Wines that do not agree with these rules may be considered as having had an addition of sugar. He suggests, however, that unconcentrated sweet wines may also be made by adding to the grape juice as soon as it begins to ferment enough alcohol to stop the fermentation. To decide, therefore, whether a wine has had an addition of sugar or been subjected to a premature interruption of the fermentation, will require a determination of glycerine.

The following table will serve to show these variations of composition :

	Tokay.	Cape Wine.	Muscatel.
Specific Gravity . . . . .	1.0729	1.0543	1.0653
Polarization { Direct . . . . .	-11.°	-6.°5	-7.°
{ After inversion -11.°		-6.°5	-7.°
{ After ferment +0°		+0°	+0°
<i>100 cc. wine contained.</i>			
Alcohol . . . . .	10.16 gms.	13.65 gms.	12.91 gms.
Extract Matter . . . . .	22.10 "	19.84 "	22.25 "
Ash . . . . .	0.26 "	0.20 "	0.26 "
Free Acid . . . . .	0.50 "	0.35 "	0.34 "
Glycerine . . . . .	0.89 "	0.13 "	0.15 "
Phosphoric Acid . . . . .	0.0292 "	0.0204 "	0.0190 "
Sugar as Grape Sugar . . . . .	19.66 "	17.51 "	20.80 "

The "Tokay" may be considered an artificially prepared wine to which sugar has been added as the composition excluding the sugar is that of a common wine. Whether the sugar was added as invert sugar or was changed by the ferment always present in young wine cannot be decided. The other wines may be considered as those in which fermentation was interrupted by the addition of alcohol. The relatively small amount of acid may be explained by the fact that grapes in southern countries contain less



acid and that a large part of the tartar has been precipitated by the alcohol.

Of course interruption of fermentation and addition of sugar may happen at the same time, and in this case a small per cent. of glycerine is often observed, especially in southern wines.

A. A. B.

**On a Source of Error in the Determination of Nitrogen in Bodies Containing the Halogens and How to Avoid It.—**

Richard Zsigmondy, *Ztschr. anal. Chem.* **28**, 58.

In using Dumas' method with Schwartz's apparatus for the determination of nitrogen in substances containing chlorine the author found that his results were constantly from 1 to 2% too high. Having observed carefully all the proper precautions he was convinced that the error was due to the halogen in the oxide of copper. As is well known cuprous chloride absorbs oxygen at from 100°–300° C., (*Jahresbericht* 1867, p. 125), and gives it off again at a strong heat. This is exactly what occurs in the usual course of these combustions. In oxidizing the reduced copper and allowing it to cool in a current of oxygen the chloride of copper absorbs oxygen forming an oxychloride, which in the subsequent operation gives off its oxygen at the high temperature. Thus oxygen enters the measuring tube with the nitrogen and vitiates the results. To prove this the author heated and then cooled the copper in a current of oxygen, replaced the oxygen with carbonic acid gas and passed the latter through the tube until all the issuing gas was absorbed by a solution of caustic potash. He then heated to redness when a considerable amount of a non-absorbable gas was evolved. This ignited a smoldering point of charcoal and was completely absorbed by alkaline potassic pyrogallate, clear proofs of oxygen. To avoid this source of error he replaced the oxygen, after the oxidation of the copper, with carbonic acid gas and allowed it to cool.

The absorption and subsequent emission of oxygen by the chloride of copper was thus avoided and as the test analyses show, the results were extremely accurate. This transmission of carbonic acid gas through the apparatus has already been proposed by Hufschmidt (*Ber. d. deutsch. chem. Gesell. z. Berlin* **18**, 1441), to prevent the adherence of air to the cupric oxide. A. A. B.

**Rapid Estimation of Fat in Milk.**—A. W. Stokes, Chem. News **60**, 214. Into special tubes, partly graduated up to 50 cc., 10 cc. of the milk, if fresh, is pipetted, and then HCl is added until the liquid stands at the 20 cc. mark. If the milk is sour, weigh out 10 gms. and wash with strong HCl into a tube until full to the 20 cc. mark. Boil the mixture till brown, allow to stand three minutes, cool by immersion in water, fill up to the 50 cc. mark with ether. Cork the tube and shake for half a minute and allow to settle for five minutes. Pipette off exactly 20 cc. of the ethereal solution into a weighed dish, evaporate off the ether, dry in an air-bath and weigh the residual fat. Notice how many cc. of ethereal solution are left, and from the whole quantity of ethereal solution originally present, the per cent. of fat in the milk is calculated. For example.

10 cc. of milk having a sp. gr. 1.031 and giving 12 per. cent. of total solids by weight, when tested as described gave in 20 cc. of ethereal solution 0.277 gms. of fat, and 6.5 cc. of ethereal solution were left in the tube, making a total of 26.5. Hence,  $\frac{.277 \times 26.5}{2} = 3.67$  per cent. in 100 cc. of the milk. Dividing this by the sp. gr. 1.031, gives 3.55 per cent. of fat by weight in the sample. Calculating from the sp. gr. and total solids gives 3.54 per cent.

A. H. W.

**On the Detection of Adulteration in Essential Oils.**—Rowland Williams, Chem. News **60**, 175. Samples of pure essential oils were obtained by the author and in each case determinations were made of the specific gravity at 60° F., potash absorption, iodine absorption, and boiling point, which results are tabulated in the article, and will be found valuable to chemists engaged in work on the essential oils.

A. H. W.

**Testing Lard for Beef Stearin.**—J. Pattison, J. Soc. Chem. Ind. **8**, 30.

Forty drops of melted lard are dissolved in 10 cc. of ether and the solution left to evaporate until crystals are formed. It is sometimes necessary to redissolve the crystals, if they have formed rapidly, by warming the solution and sometimes adding a little more ether, so as to obtain crystals which have been slowly formed. Some of the crystals are then removed with a pipette,

placed under a microscopic slide, and examined. The crystals of beef stearin form curved tufts somewhat of the shape of the short tail of a horse. The terminals should be pointed and hair-like. Lard crystals are usually formed in oblong plates, occasionally radiated, and have oblique terminals. O. O. L.

**A Rapid Method for the Estimation of Sulphur in Organic Compounds.**—W. M. Burton, *Amer. Chem. Journ.* 11, 472.

The author has modified Sauer's method of burning the substance in oxygen, and instead of passing the sulphur dioxide formed into bromine water and hydrochloric acid and then determining the sulphuric acid as barium sulphate, passes it into standard solution of potassic hydrate and titrates back with a standard acid. Tropaeoline OO which is not affected by carbonic acid or alkaline sulphites is used as an indicator. Results obtained by this process on organic compounds made in the laboratory and on crude petroleum are given which agree very closely. A cut of the apparatus used accompanies the article. C. W. M.

**A Simple Method for the Detection of Cotton Oil in Fats and in Olive Oil.**—Dr. T. Leone, *Gazz. chim. ital.* 1889, p. 355.

The author notes the wide-spread adulteration of lard in Italy and the artificial preparation of lard by a method which he has never seen mentioned. This consists in preparing all sorts of animal fats and mixing with them a certain proportion of cotton oil, the latter giving to the mixture the smell, taste and the fusibility of lard. Out of 100 samples examined in the municipal laboratory of Palermo, in the month of April, 1889, more than 75 were thus adulterated or rather artificially prepared. The method of detection of cotton oil in the mixture is as follows: Prepare an alcoholic solution of nitrate of silver containing one per cent. of nitrate of silver and one-half per cent. of free nitric acid. Pour a few cubic centimeters of the reagent into a test tube containing an equal volume of the lard under examination, and heat on a water-bath 5 to 6 minutes. The liquids form two strata, and if the lard contains cotton oil at the line of separation a yellowish brown ring will appear, otherwise no discoloration will be

observed. The reaction is sufficiently delicate to show a marked reaction when 5 per cent of cotton oil is in the lard. This reagent is equally useful for the detection of cotton oil in olive oil, and quite as delicate. Proceed in the same way, but heat the test tube containing the two liquids in the water-bath for 10 or 12 minutes. Sometimes at the line of separation of the two liquids a whitish ring appears due to the emulsion which forms, and this ring by long heating may become greenish in color owing to the presence of chlorophyl in the olive oil. This, however, need never be confounded with the yellowish brown ring caused by the presence of cotton oil.

A. A. B.

**Simple and Sensitive Method for the Detection of Mercury in Organic Liquids, Especially in Urine.**—Dr. Eugenio Brugnatelli, *Gazz. chim. ital.* 1889, p. 418.

After reviewing the various methods for the detection of mercury in organic liquids the author suggests a method based on an observation of Barford<sup>1</sup> in regard to the reduction of gold from its chloride by the vapour of mercury. The details are as follows: Take 50 cc., 100 cc., or even more of the liquid to be tested; acidulate with a few drops of hydrochloric acid and put them in a flask together with some metallic copper in turnings or powder. Place the flask over a flame, or better on a water-bath, and heat the liquid to 50°–60°. Shake the contents of the flask for about five minutes, which will cause all the mercury to precipitate on the copper. Wash the copper several times by decantation with distilled water and transfer the copper to a small glass capsule. Place on top of the copper a fragment of porcelain on which has been deposited a single drop of one per cent. solution of auric chloride. Cover the capsule by inverting over it a watch glass and place it on the water-bath. The vapour of mercury developed by the action of the heat quickly reduces the gold and on the white surface of the porcelain appear lines, spots or circles of violet-blue gold deposited in the finest possible state of subdivision. This method is capable of detecting 1-10 of a milligram of mercury in a liter of liquid. Certain precautions must be observed. 1. The copper must be strongly heated and then reduced in a steam of hydrogen to destroy all reducing organic substances. It must be

<sup>1</sup> *J. prakt. Chem. n. F.* XXXVIII, 441-472.

transferred to a bottle kept carefully closed and only removed by perfectly clean platinum or ivory pointed forceps. 2. All the apparatus must be scrupulously clean. 3. The fragments of porcelain must be washed first with chromic acid, then with distilled water, and finally strongly heated and preserved and handled like the copper. The correctness and delicacy of the method were proved by blank experiments with wine and other liquids free from mercury, when no reaction was obtained, and then by the use of extremely dilute solutions of corrosive sublimate (1-10 mg. to the liter), and of urine from persons taking mercury salts or injections of calomel when the reaction was unfailingly obtained.

A. A. B.

**Detection of Oil of Sesame in Olive Oil.**—M. W. Bishop, Chem. Zeit. Rep. 13, 282. When this oil is shaken with a mixture of equal parts sulphuric and nitric acids it gives a green color. With a freshly prepared solution of sugar in hydrochloric acid (sp. gr. 1.17) it gives a cherry red color. When two parts of this oil are mixed with three parts pure hydrochloric acid (sp. gr. 1.17) and exposed to the air and light it assumes a green color. This test is used for its detection in olive oil.

S. C.

**Estimation of the Available Extract in Malt.**—W. Schultze, Ztschr. angew. Chem. 1889, 453.

Of three methods employed in determining the amount of extract in malt reviewed by the author, he considers what he terms the "Method of two filtrates" to be the best.

The proportional method, without regard to the amount of water contained in the malt, gives results which are at least 1% too high; and the same method, when the amount of water is considered, requires too much time, apparatus and labor. The method in which the entire "malt" is used at once also requires much time and washing, and is therefore not practical when a number of samples are to be tested. In the method of two filtrates, which the author considers to be the most accurate and speedy, 50 gms. of crushed malt are treated with 200 cc. of water. After a short time this is diluted to 400 cc. and 250 cc. filtered off. This is termed the first filtrate. The remaining liquid and the residue are then washed into a porcelain dish, stirred with a glass rod, at intervals of five minutes, for over half an hour. 100 cc. are then filtered from this and termed the second filtrate. From the

specific gravity of the liquids at 15° the amount of extract is found by the Schultze-Orterman tables given in the paper.

J. E. W.

**The Estimation of Tannin by Permanganate of Potassium.**—F. Gantter, *Ztschr. angew. Chem.* 1889, 577.

1. *Necessary Solutions*—

(a.) Solution of potassium permanganate—1000 cc. = 3.988 gms.  $K_2Mn_2O_8$ , i. e., 1 cc. = 0.001 gm. tannin.

(b.) Oxalic acid solution—1000 cc. = 7.951 gms.  $C_2H_2O_4$ .

(c.) Solution of oak bark,—usually 10 gms of bark to 1000 cc. of solution.

2. *Manipulation*—

10 cc. of bark solution, after being saturated with dilute sulphuric acid, are heated to boiling and 1 cc. permanganate solution added, the color vanishing immediately. This is continued until the color disappears but slowly, when the solution is again boiled and the permanganate added drop by drop. When the precipitate which forms is not destroyed by hard boiling, 1 cc. of permanganate is added (an excess) and the solution boiled until the color disappears. Oxalic acid is then run into the solution from a second burette, until the precipitate is dissolved and the solution perfectly clear, when it is again titrated with the permanganate.

The entire amount of permanganate, after deducting the amount used up by the oxalic acid, gives the percentage of tannin.

J. E. W.

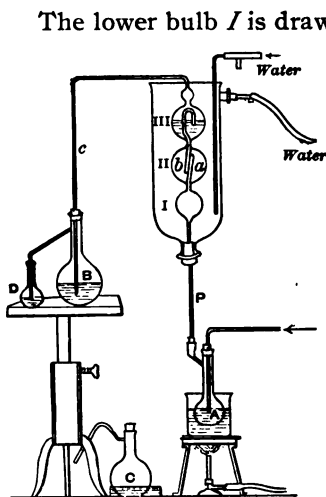
**Observations on the New Agreement as to the Method of Stating the Analyses of Wines.**—J. König, *Ztschr. anal. Chem.* 28, 202.

The author discusses the agreement of the Bavarian analytical chemists and the Imperial Board of Health Office to express the results of wine analyses in grams in 100 cc. In sweet wines whose specific gravities vary very much, a comparison is quite impossible unless the specific gravity is given and then the results will have to be calculated to percentages of weight before they can be properly compared.

As wines are sold by measure it would seem more practical to give the analyses in 100 cc. of the wine, but for scientific comparison this form of statement is worthless.

A. A. B.

**Quantitative Determination of the Methoxy Group.**—R. Benedikt and A. Grüssner, Chem. Zeit. 13, 872. The authors use a modification of Zeisel's method. Their apparatus is shown in the following cut.



The lower bulb *I* is drawn out into the tube *P* which is 25 cm. long and about 0.8 cm. in diameter. The capacity of this bulb is about 30 cc. and the two upper ones, 80–100 cc. The distilling flask *A* has a capacity of 30–35 cc. and the absorption flask *B*, 120 cc. The operation is carried out as follows: 0.5 gm. amorphous phosphorus is put into the flask *C* with a little water. The flask is attached to the tube *C* and by means of a blast the phosphorus and water are forced into the bulb *II*. The tube *C* is then washed with distilled water in the same manner and the original solution with the washings should not fill the bulb *II* more than half full. The flask *C* is replaced by the absorption flask *B* containing 50 cc. of 40% silver nitrate solution and 50 cc. 95% alcohol free from fusel oil. The smaller flask *D*, if used, contains 1 cc. silver nitrate solution and 10 cc. alcohol, but the authors have found this unnecessary. 0.2 to 0.3 gm. of the substance to be analysed is placed in the flask *A* with 10 cc. hydriodic acid (sp. gr. 1.70) and 8 cc. acetic anhydride. After passing carbon dioxide through the apparatus for some time the flask is heated in an oil bath until no more precipitate is formed in the silver nitrate solution. Any free iodine that may be formed is absorbed in the bulbs.

At the end of the operation the tube *C* is washed in the manner already described and the washings are added to the absorbing solution, which is slightly acidified with nitric acid and filtered. The washed silver iodide precipitate is then weighed and the number of methoxy groups calculated in the usual manner.

S. C.

**Analysis of Marine Oil.**—R. M. Moore, Journ. Amer. Chem. Soc. 11, 155.

The author gives the results of some analyses of oils obtained from the head of black fish and porpoise by allowing the oil to exude from the fat. The oil thus obtained is exposed to cold and the portion remaining fluid racked off. The following oils were examined by the warsh process to determine the soluble and insoluble fatty acids.

- No. 1. Porpoise jaw oil skimmed and strained.  
 No. 2. " " " " " "  
 No. 3. Porpoise jaw oil not skimmed and strained.  
 No. 4. Black fish jaw oil skimmed and strained.  
 No. 5. Black fish body oil.

	Soluble Fatty Acids.	Insoluble Fatty Acids.
1 . . . . .	17.18%	72.05%
2 . . . . .	21.44	68.41
3 . . . . .	—	96.50
4 . . . . .	21.79	66.28
5 . . . . .	2.46	93.07

The oils were next examined by Reichert's process; titrating and calculating the acidity to butyric acid.

	Reichert Figure.	Total Acidity.
1 . . . . .	47.77 cc.	17.18%
2 . . . . .	56.00 "	20.97
3 . . . . .	2.08 "	1.42
4 . . . . .	65.92 "	24.71
5 . . . . .	5.60 "	2.34

Hübl's method was then used to determine the iodine coefficient.

	Gms. Iodine per 100 Gms.
1 . . . . .	49.6
2 . . . . .	30.9
3 . . . . .	76.8
4 . . . . .	32.8
5 . . . . .	99.5

F. R. B.

**Quantitative Determination of Cellulose.**—G. Lange, Chem. Zeit. Rep. 14, 30. 10. gms. of the substance to be examined is treated with 3 or 4 parts by weight of pure caustic potash and 30 or 40 cc. of water in a tubulated retort provided with a glass stopper. The retort is gradually heated on an oil-bath until



the temperature reaches  $180^{\circ}$ , and is kept at this point for one hour. It is then removed, and after cooling to about  $80^{\circ}$  the contents are washed into a beaker, first with hot and finally with cold water. By acidifying the solution with dilute sulphuric acid a heavy flocculent precipitate is thrown down containing all the cellulose. This is made slightly alkaline with a very dilute caustic soda solution which dissolves all but the cellulose. The latter is filtered off by means of a filter pump, washed with hot and cold water, dried and weighed. The residue is then burned and the weight of the ash subtracted from the weight just obtained and the result will be the weight of pure cellulose. This method is said to be very accurate. S. C.

**A New Method for Titrating Alcohol with Chromic Acid.**—R. Bourcart, Chem. Zeit. Rep. 14, 29. The method is based on the fact that dilute alcohol heated at  $100^{\circ}$  with a dilute solution of potassium bichromate and sulphuric acid is gradually but completely converted into acetic acid.  $\frac{2}{3}$  of a molecule of bichromate is used for every molecule of alcohol, and the mixture is placed in a tube which is closed by melting together or with a rubber cork securely fastened. After heating two or three hours in boiling water it is allowed to cool and sufficient potassium iodide is added to keep the free iodine in solution. The free iodine is then titrated with thiosulphate solution in the usual manner. The chrome alum formed does not interfere with the sharpness of the reaction.

The strength of the solutions are as follows:

Potassium bichromate . . . . .	0.5 % solution.
Sulphuric acid . . . . .	25. " "
Potassium iodide . . . . .	10. " "
Starch . . . . .	2. " "
Alcohol about . . . . .	0.5 " "

For analysis, 10 cc. alcohol solution are used with 50 cc. bichromate and 10 cc. of the sulphuric acid.

The same method is used for titrating aldehyde except that  $\frac{1}{3}$  of a molecule of bichromate is used for every molecule of aldehyde. S. C.

**The Examination of Commercial Glycerine.**—J. H. Wainwright, Journ. Amer. Chem. Soc. 11, 125.

To distinguish crude from refined glycerine, the author's two

most important tests are the silver nitrate and lead tests. These are made as follows: 5 cc. of the sample is dissolved in 20 cc. distilled water in a large test tube, and 5 cc. of a 2 per. cent. silver solution added. This is shaken and allowed to stand for one hour. In refined glycerine a darkening of the solution may occur, but if not very heavy the sample may be considered refined. In crude glycerine a considerable precipitate forms. The lead test consists of treating one part of glycerine with one of water and two of lead solution (10 gms. lead acetate and 8 gms. of litharge in 500 cc. water, boiling and filtering). This is shaken and allowed to stand as before. Refined glycerine remains unchanged or only shows a slight coloration and never a flocculent precipitate. Ammonia, ammonium, oxalate, barium chloride, nitrogen peroxide gas, and Fehling's solution have no effect on refined glycerine.

F. R. B.

**The Amount of Nitric Oxide Formed in the Combustion of Organic Substances.**—F. Klingemann, (Ber. 22, 3064.)

The author has burned a considerable number of organic substances, using the method devised by Frankland and Armstrong, (J. Chem. Soc. 21, 109), and determined the amount of NO formed. The largest amount obtained was with the azine  $C_{20}H_{12}N_2$ , which gave 10.28%. The results are of little apparent value, as no correspondence between composition and yield of NO is apparent from the figures given.

E. H.

**Ash Determination.**—F. A. Flückiger, Ztschr. anal. Chem. 27, 637. The substance is carefully heated in a platinum or porcelain dish until it is completely carbonized without having caused it to burst into a flame. This is done by covering the dish with some platinum gauze. When the volatile matter is all driven off, the residue is treated with water, evaporated to dryness, and gradually ignited to a white ash. If the ash still contains carbon, the operation must be repeated.

S. C.

**The Determination of Fat in Linseed Oil-Cake.**—R.

Klopsch (Ztschr. anal. Chem. 27, 452.) If linseed oil-cake is dried at a temperature of over  $100^\circ$ , or if heated for a long time at  $100^\circ$  the fat can no longer be completely extracted with ether. When dried at  $105^\circ$  for six hours not more than half the fat can

be extracted, and when dried at  $110^{\circ}$  for the same length of time only about a third can be obtained. This is apparently due to surface oxidation of the oil particles over which a skin insoluble in ether forms. A temperature of  $100^{\circ}$  for three hours (water bath) does no harm, and this is sufficient to dry the cake perfectly. That the full amount of fat is thus obtained was proved by comparison with the amount formed by drying the same samples in an atmosphere of pure hydrogen and then extracting the fat. E. H.

**Determination of Cane Sugar in Liquers, Confectionery and Chocolate.**—E. Rathgen (Ztschr. anal. Chem. **27**, 433). The sugar determination was made by a Soleil's or a Schmidt & Hensch saccharimeter with 200 mm. tube. If 26.048 gms. substance are weighed out and dissolved in water to make 100 cc. and polarized in a 200 mm. tube, the number of degrees of rotation expresses also percentage amounts of sugar.

If half the amount is taken and made up to 100 or 200 cc., the result obtained must be multiplied by 2 or 4.

The substance to be polarized must first be tested for grape sugar by warming the solution with a little copper sulphate and caustic soda. If no precipitate of cuprous oxide forms, the polarization may be proceeded with; but if a precipitate forms, Clerget's inversion process must be used. For this purpose, 50 cc. of the solution is used for direct polarization, and the remaining 50 cc. treated with 5 cc. concentrated HCl, heated in a water bath for 15 minutes to  $67^{\circ}$ – $70^{\circ}$ , then cooled to the ordinary temperature, diluted to 100 cc., and polarized. In polarizing, the temperature  $t$  must be determined. If  $A$  is the rotation of the original solution and  $B$  that after inversion, both taken for 26.048 gms. substance and a 200 mm. tube, the percentage of cane sugar may be calculated by means of Clerget's formula

$$R = \frac{100 (A - B)}{142.4 - \frac{1}{2} t} \quad (1)$$

in which, because ordinarily  $A$  is plus and  $B$  is minus, the difference  $A - B$  becomes the sum of the two readings. With mixtures of cane and grape sugar, the rotation may be dextro also after inversion. In this case, reading  $B$  must of course be subtracted from reading  $A$ .

In liquers, the amount of sugar in grams contained in one liter is given. A measured volume  $V$  (25 or 50 cc. of the liquer) is therefore diluted to 100 cc. and polarized. The cane sugar is then found by means of the formula.

$$\text{Grams cane sugar in a liter ; } r = \frac{26.048 (A - B)}{(42.4 - \frac{1}{2}t) V} \quad (2)$$

If the temperature is kept at  $20^\circ$  when reading, this formula may be simplified so as to read

$$r = 196.7 \frac{A - B}{V}$$

In certain manufactured articles like preserved fruits, fruit jelly, marmalade, etc., a part of the cane sugar used will have been transformed by the organic acids into invert sugar.

The analysis by Clerget's process and calculation by formula (1) or (2) gives the amount of cane sugar present at the time the determination is made. If, however, it is desired to know how much cane sugar was originally present, this may also be calculated from the left-handed rotation  $B$ . This is on the supposition that no invert sugar was originally present. 26.048 gms. cane sugar dissolved in water and made up to 100 cc. after inversion gives in a 200 mm. tube a left-handed rotation of  $42.4 - \frac{1}{2}t$  degrees. The amount of left-handed rotation found,  $B$ , will then correspond to  $\frac{26.048 B}{42.4 - \frac{1}{2}t}$  cane sugar and the whole original percentage of cane sugar present  $R_1$  will then be

$$R_1 = \frac{100 B}{42.4 - \frac{1}{2}t} \quad (3)$$

If  $t = 20^\circ$  this becomes

$$R_1 = 3.086 B$$

In liquers the number of grams of ( $r_1$ ) cane sugar originally present in a liter may be found by the formula

$$r_1 = \frac{26048 B}{(42.4 - \frac{1}{2}t) V} \quad (4)$$

where  $V$  is the volume of liquer in cc. which was made up to 100 cc. If the temperature  $t$  is  $20^\circ$  this becomes

39147A

$$r_1 = 804 \frac{B}{V}$$

In preparing solutions of confections consisting for the most part of cane sugar, the material may be weighed directly into the measuring flask. When a considerable insoluble residue is present it is best to dissolve and filter into the measuring flask. According to the necessities of the case, the solution is made up either to 100 or 200 cc. In far the larger number of cases the solutions are too turbid for polarizing. As clearing reagents aluminum hydroxide, prepared by precipitating aluminum sulphate with ammonia, washing carefully, and stirring with water until the mixture has the consistence of syrup, is one of the best. 2 to 3 minutes shaking with this substance followed by filtration always gives a clear solution. Lead acetate and alum are used only with chocolate, together with the aluminum hydroxide. Colored liquids are decolorized by shaking with blood charcoal.

#### LIQUERS.

Since the alcohol present has no influence, liquers may be polarized directly, provided invert sugar is absent. If this is present, however, double polarization must be resorted to, and as alcohol has a disturbing influence in this case, it must first be removed by evaporation. If the liquer has an acid reaction, it should be neutralized with a few drops of ammonia and then evaporated to half its volume. If direct polarization only is necessary, the number of gms. cane sugar per liter,  $r$ , may be found by the formula

$$r = 2.6048 A$$

where  $A$  is the rotation in degrees.

#### CONFECTIONS.

In gum drops and caramels the cane sugar cannot be determined satisfactorily on account of the gum in the first and starch sugar in the second, both of which are optically active. In order to extract the sugar from candied fruits, they are cut in fine slices, soaked in water to which a little ammonia has been added, and filtered through muslin. Pastes and jellies are rubbed up in a mortar with ammoniacal water. The pectin substances present

have no influence upon the rotatory power of the cane and fruit sugar.

#### CHOCOLATE.

13.024 gms. of the rasped chocolate is moistened with alcohol, 30 cc. water added, and warmed for 15 minutes on the water bath. It is then poured upon a muslin filter and washed with hot water into the measuring flask. The turbid liquid is treated with 5 cc. lead acetate solution, shaken, and after standing several minutes, a few drops of alum solution and a little aluminum hydroxide added and the flask filled to the mark. After shaking vigorously, the solution is filtered through a slightly moistened folded filter. The first few drops usually run through turbid. E. H.

**Estimation of Fatty Acids in Alizarin Oil.**—Fred. Guthrie, Chem. News, **61**, 52. About 5 gms. of oil are weighed out in a small beaker, washed by means of a little water into a 6 oz. flask, and boiled slowly for half an hour, after the addition of 10 cc. of normal caustic soda. 20 cc. of normal sulphuric acid are now added and the flask is heated for about half an hour on a water-bath. The contents of the flask are now filtered through a tared Swedish filter and the flask is thoroughly rinsed out with boiling water, and the washings added to the filter. The fatty acids after being washed free from acid by boiling water, are removed with the filter paper to a tared platinum capsule and dried at 212° F. until the weight is constant. The advantages which are claimed for the above method are:

(1.) The sulpho-fatty acids being decomposed and the sulphuric acid being washed away, the fatty acids do not decompose or blacken when dried.

(2.) The fatty acids, being practically insoluble in boiling water, can be washed well from the acid used to liberate them.

(3.) Any free oil which the alazarin may contain is saponified and weighed as fatty acid. A. H. W.

**Detection of Saccharin.**—Chem. Cent. 1889, **2**, 615.—The method used by the chemists of the French Customs Office is as follows; 20 gms. of the substance to be examined is dissolved in an equal bulk of water and shaken to mix it. 5 drops sulphuric acid are then added and an equal volume of ether. The mixture

is shaken carefully in order to avoid danger of forming an emulsion, and after allowing to stand for some time the ether is separated, evaporated, and the residue tested by the taste. If this is sweet saccharin is present.

E. H.

**Determination of Boric Acid in Wine.**—S. Weinwurm (Chem. Cent. 1889, 2, 939) finds that Rippert's method for the detection of boric acid in wine is satisfactory only when a liter of the wine is evaporated, and a turmeric solution used in place of turmeric paper. Boric acid is usually present in wine only in traces.

E. H.

**Determination of Free Tartaric Acid in Vinegar.**—A. Jolles (Chem. Cent. 1889, 2, 944). 5 cc. of the vinegar is diluted to a liter, and 5–20 cc. of the solution, according to the strength of the vinegar, is run into a cylinder of white glass of such diameter that the liquid fills the glass to a height of 18–20 cm. 2 cc. of a 1%  $\text{Fe}_2\text{Cl}_6$  solution is then added and the resulting color compared with that obtained by using a pure 0.1% tartaric acid solution. The upper limit for this method of testing is 0.006 gm. tartaric acid in 100 cc. Colored vinegar must be decolorized before the method can be used. Acetic acid acts upon the ferric solution only when it contains over 10% acetic acid.

E. H.

**Determination of Ash in Sugars.**—J. V. Grober (Chem. Cent. 1889, 2, 994). To avoid the difficulty in burning off the carbon by simple ignition, the author mixes 2–5 gms. of the sugar with pulverized oxalic acid, and burns in a platinum dish of sufficient size. The mass melts at first, boils, turns yellow, then brown, and finally deep black. The combustion of 2 gms. crude sugar can be completed in half an hour. If the mass appears to burn less rapidly in some places, it is well to shake a little pulverized acid over them. If black specks are left in the ash, they should be moistened with ammonium nitrate and again ignited.

E. H.

**Determination of Fat in Milk, Cream, Etc.**—W. Schmid (Ztschr. anal. Chem. 27, 464). 5 cc. cream or 10 cc. milk is placed in a 50 cc. cylinder divided in tenths, 10 cc. concentrated hydrochloric acid added and boiled, shaking constantly until the liquid becomes dark brown. It is then cooled, 30 cc. ether added,

shaken, allowed to stand, 10 cc. of the ether drawn out with a pipette, evaporated on the water bath, then dried at 100° in the air bath, and the residue weighed. From the weight obtained, the entire amount of fat present is easily and rapidly calculated. If the process is properly performed, the ether and water separate perfectly, without the slightest turbidity. The results obtained are exact, not differing by a tenth per cent in duplicates and agreeing equally well with results obtained by ordinary gravimetric methods. The time required is not more than fifteen minutes with proper facilities.

E. H.

**Determination of Ash in Raw Sugars.**—E. G. Weichmann, Sch. of Min. Q., Nov. 1889. The author has examined the results obtained by Scheibler's process and finds that when 10% is subtracted, as directed by Scheibler, the results obtained are too low, while if taken without deduction, they are very near the truth. He suggests the acceptance as a working factor of the sulphate ash actually obtained.

E. H.

**Gravimetric Determination of Thiocyanates.**—H. Alt (Ber. 22, 3258). Barium chloride is added to the solution and then nitric acid. On warming this the cyanate is decomposed and hydrocyanic and sulphuric acids are formed, the latter being precipitated as barium sulphate, which is weighed and the thiocyanate calculated. One equivalent barium sulphate corresponds to one equivalent thiosulphate. A solution which gave 1.39 per cent. thiocyanate according to Volhard's process, gave by the new method 1.32 and 1.35 per cent.

E. H.

**Method of Determining Indigotine for Commercial Purposes.**—F. A. Owen (Jour. Am. Chem. Soc. 10, 178). One gram of the sample is dried at 100° C. When dry it is transferred to a mortar, a little water added, and ground to a thin paste. This is washed into a 250 cc. graduated flask. To this is added 3 gms. zinc dust and about 6 gms. NaOH, and then filled a little above the mark. The flask is shaken occasionally, and when reduction is complete, the solution has a green color. 50 cc. of the clear liquid is drawn off, allowed to stand exposed to the air half an hour, acidified with hydrochloric acid, filtered through a carefully washed filter, dried at 100° C., and weighed.

F. R. B.



**Comparative Results in the Analysis of Fats.**—R. W. Moore (Jour. Amer. Chem. Soc. 11, 144). The author uses the modification of Reichert's process proposed by Dr. Waller (Jour. Am. Chem. Soc. 8, 155, which consists of saponifying 2.5 gms. of fat with 1 gm. of caustic potash and 50 cc. of 70% alcohol. After saponification, the alcohol is completely driven off, the last portion being removed by a current of air. The soap is then dissolved in 50 cc. hot water and decomposed with 20 cc. dilute sulphuric acid (1.10). The flask is now connected with a condenser furnished with a bulb tube to prevent mechanical carrying over of the acid. 50 cc. are distilled off and titrated with  $\frac{n}{10}$  NaOH. This furnishes the Reichert figure. 50 cc. water are added to the contents of the flask, the distillation continued, and the distillate titrated. This is continued until a neutral distillate of 50 cc. is obtained. The total acidity of all the distillate is now calculated as butyric acid. The total per cent. of volatile fatty acid is thus obtained. The insoluble fatty acid remaining in the flask is filtered from the oil. The fatty acids are washed with hot water until free from acid. The condenser is then rinsed with hot alcohol and added to the contents of the flask. The alcohol is now driven off, and the oil dried at 105° C. to constant weight. The per cent. of insoluble fatty acid can then be calculated. The following table (Jour. Am. Chem. Soc. 8, 155) gives a comparison of the results :

*Comparison of Wash and Waller's Process on Butter.*

	Wash Process.		Waller's Process.	
	Per cent. Soluble. Acid.	Per cent. Insoluble. Acid.	Per cent. Soluble. Acid.	Per cent. Insoluble. Acid.
Dairy Butter, November,	5.42	87.71	5.61	87.74
Holstein "	5.11	89.00	5.28	88.96
Native "	5.76	87.09	5.80	87.10
Durham "	6.86	87.79	6.86	87.76
Jersey "	6.37	87.67	6.30	87.54
Rancid "	6.53	88.48	6.49	88.56

F. R. B.

**The Behavior of the Quinine Alkaloids towards Xylene and Mayer's Reagent.**—(Chem. Cent. 1889, 2, 615.) The solubility of the quinine alkaloids in commercial xylene (b. p. 136–139°) was found to be as follows :

1 part quinine dissolves at	15°	in	909 parts xylene.
" " " "	138°	"	155 " "
" cinchonine " "	15°	"	7407 " "
" " " "	138°	"	170 " "
" quinidine " "	15°	"	211 " "
" " " "	138°	"	8 " "
" Cinchonidine " "	15°	"	2022 " "
" " " "	138°	"	7.8 " "

Mayer's solution (13.546 gms.  $\text{HgCl}_2$  and 49.8 gms. KI in a liter of water) behaves as follows :

1 cc. corresponds to	0.0106 quinine.
" " "	" 0.0092 quinidine.
" " "	" 0.0079 cinchonine.
" " "	" 0.0091 cinchonidine.

**A Method for the Examination of Meat Extracts.**—H. N. Warren, Chem. News 61, 15. The dried extract, to which a known quantity of carefully prepared sand has been added, is placed in a tared filter paper, previously treated with alcohol. The whole is then placed in a platinum cage, made by coiling a piece of platinum gauze spirally and turning inwards the lower extremities to form a bottom, while the top is furnished with a cap surmounted by a hook. The cage is placed inside a glass tube of the requisite caliber and the usual connections made for an extraction.

The same apparatus is recommended for milk analysis, after the following method. A sufficient amount of the sample is evaporated to a convenient bulk in a platinum dish, and then poured on a weighed quantity of prepared sand, when it is retained without danger of loss, and may be dried to a constant weight. Prepared sponge was also used with advantage as an absorbing agent.

A. H. W.

**Simultaneous Estimation of Carbon and Sulphur in Organic Substances.**—M. L. Prunier (Comptes rendus 109, 904). The author's method consists of heating 1 part of the material with 80 or 100 parts of potassium permanganate in a combustion tube. The gas from the combustion is first passed through a solution of potassium permanganate and then through baryta water. When the combustion is complete, the precipitated oxide of manganese is filtered from the permanganate solution, the fil-

trate acidified with hydrochloric acid, and the sulphur precipitated with barium chloride. To the baryta solution sulphuric acid is added, and the solution heated. The  $\text{CO}_2$  which is liberated is determined in the usual way, and calculated to C. F. R. B.

## ATOMIC WEIGHTS.

EDITED BY F. W. CLARKE.

**Oxygen.**—Cooke describes a new method for the determination of gaseous densities, by means of which the Rayleigh correction to the tare of the glass globes may be avoided. The globe to be calibrated is filled with carbon dioxide, which is then drawn off into absorption tubes and weighed. The tare is thus ascertained directly. With globes thus tared the specific gravity of hydrogen, in three concordant experiments, was .06962 in average. Taking Regnault's specific gravity of oxygen, as corrected by Crafts, 1.10562, we get 15.882 for the ratio between the two quantities. The value previously found by Lord Rayleigh was 15.884.—*Am. Chem. Journ.* 11, 509.

**Palladium.**—In this Journal, Vol. II, p. 353, Keiser's determination of this atomic weight was given. Eleven experiments upon the amount of Pd. in  $\text{Pd}(\text{NH}_4\text{Cl})_2$  gave in mean Pd. = 106.352. Keiser now gives an additional series of eight similar experiments, as follows:

2.61841	salt gave	1.31900	Pd.
2.23420	" "	1.12561	"
1.73553	" "	.87445	"
1.69160	" "	.85210	"
1.72403	" "	.86825	"
1.12222	" "	.56535	"
1.17457	" "	.59200	"
2.42760	" "	1.22280	"
Sum. . . . .	14.72816	7.41956	

Hence, in mean, Pd. = 106.350, with a maximum of 106.455, and a minimum of 106.286. The mean of both series is 106.351.—*Am. Chem. Journ.* 11, 403.

**Gold.**—The experiments of Mallet, already referred to in this journal, have at last been published in full. Seven series were made, as follows:

1. A neutral solution of auric chloride was divided into separate portions by weight. In one portion, the gold is precipitated by pure sulphurous acid, and weighed. In another portion, approximately equal, the chlorine was precipitated by a standard solution of silver, after the method of Stas. In this way the ratio Au : Ag<sub>3</sub> was repeatedly determined, with the subjoined results :

	7.6075 grammes Au.	=	12.4875 Ag.
	8.4212 " "		13.8280 "
	6.9407 " "		11.3973 "
	3.3682 " "		5.5286 "
	2.8244 " "		4.6371 "
Sum . . . . .	29.1620 " "		47.8785 "
Ag <sub>3</sub> : Au :: 322.98 : x.			

2. A similar series of experiments with auric bromide gave results as follows :

	8.2345 grammes Au.	=	13.5149 Ag.
	7.6901 " "		12.6251 "
	10.5232 " "		17.2666 "
	2.7498 " "		4.5141 "
	3.5620 " "		5.8471 "
	3.9081 " "		6.4129 "
Sum . . . . .	36.6678 " "		60.1807 "
Ag <sub>3</sub> : Au :: 322.98 : x.			

3. A carefully purified potassium auric bromide, KAuBr<sub>4</sub>, was treated similarly, and the following data obtained :

	5.7048 Au.	=	12.4851 Ag.
	7.9612 " "		17.4193 "
	2.4455 " "		5.3513 "
	4.1632 " "		9.1153 "
Sum . . . . .	20.2747 " "		44.3710 "
Ag <sub>4</sub> : Au :: 430.64 : x.			

4. Weighed quantities of trimethyl-ammonia aurichloride, N(CH<sub>3</sub>)<sub>3</sub>HAuCl<sub>4</sub>, were decomposed by heat, and the weight of residual gold determined. Results as follows :

	14.9072 salt gave	7.3754 Au.
	15.5263 " "	7.6831 "
	10.4523 " "	5.1712 "
	6.5912 " "	3.2603 "
	5.5744 " "	2.7579 "
Sum . . . . .	53.0514 " "	26.2479 "
NC <sub>3</sub> H <sub>10</sub> Cl <sub>4</sub> : Au :: 201.40 : x.		

5. Gold and silver were simultaneously precipitated by electrolysis.

	5.2721	Au. =	2.8849	Ag.
	6.3088	"	3.4487	"
	4.2770	"	2.3393	"
	3.5123	"	1.9223	"
	3.6804	"	2.0132	"
Sum . . . . .	23.0506	"	12.6084	"

Ag. : Au. :: 107.66 : x.

6. Gold, precipitated by electrolysis was compared with the amount of hydrogen liberated simultaneously by the same current.

	4.0472	grammes Au.=	0.02053	H.
	4.0226	"	.02039	"
	4.0955	"	.02079	"
Sum . . . . .	12.1653	"	.06171	"

H. : Au. :: 1 : x.

7. Gold was precipitated by metallic zinc, and weighed, solutions of chloride or bromide being used. The amount of hydrogen liberated by the solution of a known quantity of the same zinc was also determined, and thus the ratio Au : H<sub>2</sub> was ascertained.

	10.3512	grammes Au.=	0.15768	H.
	8.2525	"	.12574	"
	8.1004	"	.12345	"
	3.2913	"	.05016	"
	3.4835	"	.05306	"
	3.6421	"	.05550	"
Sum . . . . .	37.1210	"	.56559	"

From these experiments the following values for the atomic weight of gold are calculated, when H = 1, Ag = 107.66, Cl = 35.37, N = 14.01, and C = 11.97.

	Highest.	Lowest.	Sum.
1st Series . . . . .	196.770	196.688	196.722
2d " . . . . .	196.843	196.731	196.790
3d " . . . . .	196.817	196.685	196.775
4th " . . . . .	197.289	197.131	197.225
5th " . . . . .	196.945	196.709	196.823
6th " . . . . .	197.283	196.994	197.137
7th " . . . . .	196.956	196.848	196.897

The general mean of all the 34 experiments is Au = 196.910.  
—*Phil. Trans.* 180, pp. 395-441.

## PHYSIOLOGICAL CHEMISTRY.

**The Determination of Nitrogen in Urine.**—P. Cazeneuve and L. Hugouneng, Bull. soc. chim. **49**, 901. The method described in note on page 77 is recommended for the determination of the total nitrogen in urine. Neither the Kjeldahl nor the soda lime method is found to be reliable in the analysis of a mixture so complex as urine. For the determination, 5 cc. of urine is mixed with 5 gms. of dried plaster of Paris, and .05 gm. oxalic acid added. After desiccation in the air bath, the mass is ground up and intimately mixed with 30 gms. of cupric oxide; the whole is then placed in the combustion tube, and the operation completed in the usual way.

I. A. P.

**The Determination of Albumen in Urine.**—H. Schaumann, Ztschr. anal. Chem. **27**, 635. The precipitated albumen is filtered through a layer of purified cotton contained in a drawn-out glass tube, with the aid of the filter-pump; the tube is dried at 100° and then at 110°, a current of air being drawn through it constantly until the weight remains constant. The amount of urine taken should be so regulated that the albumen does not exceed 0.2 gm.

E. H.

### **Recent Researches on Ptomaines.**—

(1.) *Immunity against Septicaemia induced by Soluble Substances.*—(Roux et Chamberland, Annales de l'institut Pasteur 1888). Cultures of the bacillus of malignant oedema in bouillon were sterilized by being heated to 105° to 110° for 10 minutes, filtered, and portions of the filtrate were injected every third day into the abdominal cavities of Guinea-pigs. The injection produced some disturbances, but the subsequent ones were borne without apparent effect. Two days after the last injections these animals, together with others used as controls, were inoculated with the virulent germs of malignant oedema. All of the control animals died within 18 hours, but those which had received the sterilized cultures remained permanently unaffected.

A second series of experiments seems to show that heating the culture to 105° to 110° partially decomposes the chemical poisons. The serose fluids collected from the tissues of Guinea-pigs dead from malignant oedema were rendered germ-free by filtration

through porcelain cells. 40 cc. of this killed healthy animals within a few hours with all the characteristic symptoms of malignant œdema, while the same amount of the heated culture had been borne. Seven or eight inoculations with 1 cc. of the filtered fluid secured immunity against subsequent inoculations with the germs.

They also show that cultures of the germ in certain media do not produce chemical substances which may induce immunity. This emphasizes the fact that the chemical products of putrefaction depend upon the medium in which the germ grows as well as upon the nature of the germ itself.

(2.) *Immunity Against Charbon Symptomatique Induced by Soluble Substances.*—(Roux, *ibid*). Experiments similar to the above demonstrate that the germ of charbon symptomatique as well as that of malignant œdema produces a chemical poison, and the establishment of a tolerance for that poison gives for a time at least immunity against the germs.

(3.) *The Value of Iodoform in the Dressing of Suppurating Wounds.*—Behring (*Deutsche Medicinische Wochenschrift*, 1889, 653) claims that the value of iodoform is not due to its germicidal properties, but to the fact that it renders chemically inert the ptomaine, cadaverine. This position is supported by de Ruyter (*Fortschritte der Medicin*, 1888, 773) and by Warle (*Transactions Michigan State Medical Society*, 1889).

(4.) *The Ptomaine of Hydrophobia.*—Aurep (*Proceedings of the Medical Society of St. Petersburg*, 1889) has obtained by Brieger's method from the brains of rabbits, in which hydrophobia had been induced, an alkaloidal body possessing highly poisonous properties. From one hundred brains he isolated 0.05 gm. of the substance. The ptomaine and its salts crystallize in water. The chemical composition has not been determined. Small doses (0.00001–0.00003 gm.) produce in animals (rabbits) an elevation of temperature, restlessness, rapid breathing and palpitation of the heart. Medium doses (0.00005–0.0002) produce difficult respiration, tremor, weakness of the heart, and general loss of strength. Large doses (0.0003–0.0005 gm.) are followed by depression of temperature, paralysis of the extremities, salivation, and death with the symptoms of asphyxia. It is claimed that in

these symptoms we have the complete chemical history of hydrophobia, the effects of the smaller doses corresponding with the first, and those of the larger doses with the later stage of the disease.

(5.) *The Presence of a Chemical Poison in Cultures of the Germ of Peripneumonia of Oxen.*—Arloing (Comptes rendus 106, 1) finds that if cultures of this germ be injected under the skin of oxen, an inflammatory tumor appears at the point of inoculation and increases in size for two or three days, after which it gradually disappears. However, it can often be recognized twenty or thirty days after the inoculation. The same effect is produced by the injection of sterilized cultures. From this it seems evident that the active agent is a chemical poison.

(6.) *Studies of Fugu-Poison.*—Takahashi and Moko (Centralblatt für die med. Wissenschaften, 29 und 49, 1889.) State that it is well known that certain species of fish in Japan are poisonous. The best known of these fish is the fugu, and in this the chief deposit of the poison is in the ovaries, and cases of poisoning are not rare. With rabbits, dogs and cats the fugu-poison produces paralysis of the nerve centers in the medulla. The respiration becomes slow and finally ceases without convulsions. The heart-beat becomes slower and slower, but remains regular until it ceases altogether.

The poison is soluble in water, difficultly soluble in absolute alcohol, insoluble in ether, petroleum-ether, chloroform, and amylic alcohol; it is not decomposed by prolonged boiling, is not precipitated by lead acetate, mercuric chloride, platinum chloride and other alkaloidal reagents. It diffuses rapidly through animal membranes.

(7.) *Ptomaines from Mixed Typhoid Cultures.*—Vaughan, (Journal of the American Medical Association, Dec. 14, 1889), states as follows: I began last December a chemical study of typhoid stools with especial reference to the presence of ptomaines in the same. However, I soon met with great difficulty. In the first place, it was not easy to always have at hand material in sufficient quantity, and although friends practicing where epidemics of the disease existed, kindly took the trouble to endeavor to sup-



ply me, this difficulty alone was sufficient to cause me to alter my plans. Moreover, the coloring matter present was taken up by my solvents and it proved no light task to exclude them.

I finally adopted the following method: The stools were received directly from the patient in a sterilized vessel. With a sterilized platinum needle flasks of meat broth previously sterilized were inoculated with these stools. These flasks were then kept at a constant temperature of from  $38^{\circ}$  to  $40^{\circ}$  C. for varying periods of time, after which I attempted to isolate any ptomaines that might be present. Thus, it will be seen that I worked with a mixed culture containing all the germs present in the fæces; the object being to ascertain whether or not the basic substance or substances formed in such cultures would differ from the ptomaine of Eberth's bacillus.

The method of isolating the ptomaine was as follows: After the cultures of meat broth had been kept in the incubator at a temperature of from  $38^{\circ}$  to  $40^{\circ}$  C. for from ten to twenty days they were filtered and rendered feebly acid with hydrochloric acid. I may say here that the cultures were invariably ammoniacal. The acidified filtrate was then evaporated to dryness, or as nearly to dryness as could be done, on the water-bath. The residue was then extracted with absolute alcohol, the extract precipitated with an alcoholic solution of mercuric chloride, saturated at the temperature of the water-bath, the precipitate was collected, washed with alcohol, suspended in distilled water, and decomposed with hydrogen sulphide. The mercuric sulphide was removed by filtration, the filtrate evaporated to dryness on the water-bath and this residue extracted with absolute alcohol, the extract precipitated with a solution of platinum chloride in absolute alcohol, the precipitate collected, washed with absolute alcohol and dissolved in distilled water. The aqueous solution was concentrated on the water-bath until the platinum compounds began to crystallize out. This aqueous solution contains two or more platinum compounds, but so far I have given my attention to only one of them. This forms in rhombic prisms, which are purified by repeated resolution and recrystallization. For purposes of physiological experimentation, this platinum salt was decomposed with hydrogen sulphide and the filtrate concentrated nearly to dryness on the

water-bath, when the crystals form. This is the hydrochloride of the ptomaine.

The following experiments show the action of this ptomaine: February 6, 1889. An aqueous solution, neutral in reaction, of this ptomaine was injected under the skin over the abdomen of a dog at 2.50 P. M. The temperature of the rectum before the injection was 100.5°. At 3.35 the temperature was 102.6°, at 4.10, 103.2°. About this time severe purging set in and continued with intermissions and prolonged straining for an hour. At 4.35 the temperature was 103.4°; at 5, 103.9°; at 5.30, 104°; at 6, 103.9°. The temperature was not taken again until 9 A. M. February 7, when it was found to be 102°; at 12, 101.9°; at 6 P. M. 100.5°. Between 2.50 P. M. and 5.30 P. M., or within two hours and forty minutes, the temperature of this animal went up 3.5°. The straining and purging were also marked.

May 18, 1889, I gave by the mouth an aqueous solution of the crystals to a dog which weighed 15 lbs. The rectal temperature before the administration of the poison was 101°, the time of administration, 3 P. M. At 3.15 retching and vomiting set in and continued at intervals for more than two hours. At 3.30 the temperature was 103°, an elevation of 2° within one half-hour. At 3.55 the animal began to purge. The first discharges contained much fæcal matter, but the subsequent ones were watery and some of them contained mucus plainly stained with blood. At 4, the temperature was 103.5°, and remained the same at 4.30. The animal was not seen again until 10 A. M. the next day, when the temperature was 100.5° and recovery seemed complete.

I have records of other experiments with this ptomaine, but as they are repetitions of the above in general, I will not detail any more at present.

I should not place any great stress upon the elevation of temperature were that the only symptom, but when taken with the gastro-intestinal disturbance I think that I have some reason for hoping that the discovery of this ptomaine may prove of value in elucidating the etiology of typhoid fever. Of course, further experimentation is necessary. It remains to be seen whether or not typhoid stools invariably contain germs capable of producing this chemical product, also whether or not the same germs

are contained in normal stools or in those of any other disease than typhoid fever. Moreover, I hope by means of making plate cultures to determine whether this ptomaine is the result of the activity of a single germ or two or more microorganisms. I may say that the stools used in these experiments were from undoubted cases of typhoid fever and from three widely separated outbreaks of the disease.

Some of the conditions influencing the formation of this poison may be of interest. It was found most abundantly when the cultures were kept at a temperature of 40° C. for a period of ten days. After this time the amount of the yield grows less, though I have found traces after twenty days. I obtained larger quantities from cultures made on pork broth than from those made upon beef broth, though the poison was never absent from the latter. From 6 quarts of pork broth I obtained as the greatest yield nearly 2 grams of the platinum compound. Though I have made several partial ultimate analyses of the platino-chloride I am not yet ready to give a formula for this base, nor do I care to propose a name for it at present.

The platino-chloride crystallizes in fine rhombic prisms and the hydrochloride in red needles. The red color seems to be inherent to the substance and not due to impurities. The hydrochloride obtained from the decomposition of the mercury compound has the same color as that from the platinum compound."

**Determination of Albumen in Urine.**—H. Schaumann, *Ztschr. anal. Chem.* **27**, 635. Instead of filter paper, the author used a filtering tube, containing some purified cotton, such as is used in the gravimetric analysis of sugar. This tube is dried at 110° and weighed. The albumen in the urine is precipitated by the addition of a little acetic acid and heating half an hour on a water bath. The clear liquid is then poured through the filtering tube and the precipitated albumen is washed with hot water, first by decantation, and finally in the filtering tube by the aid of a filter pump, until the washings give no reaction with silver nitrate. The wide end of the filtering tube is closed with a cork through which passes a small glass tube. This tube is connected with a potash bulb containing concentrated sulphuric acid, and

the other end of the filtering tube is attached to a calcium chloride tube. The filtering tube is placed in a suitable air-bath and heated for an hour at  $100-110^{\circ}$ , while air is drawn through the whole arrangement by means of an aspirator or filter pump. When the contents of the tube are dry they are weighed, and the difference between this weight and the one previously taken, gives the weight of the albumen. The author claims that this is a much more rapid method than where filter paper is used. He also mentions as a source of error the loss of albumen which may occur if the cotton is packed too loosely in the filtering tube. S. C.

**The Relative Value of Different Pepsin Tests.**—J. H. Stebbins (Jour. Am. Chem. Soc. **10**, 63). Of the different pepsin tests, the author considers the Kremel test the most accurate. It is made as follows: 1 gm. of egg albumen is dried at  $40^{\circ}$  C. and pulverized, and 0.1 gm. of the pepsin to be tested, are put into a 100 cc. flask and dissolved in 50 cc. of 0.2 per cent. hydrochloric acid. The solution is heated for three hours at  $38-40^{\circ}$  C. and then neutralized with sodium carbonate, heated on a water bath to  $90^{\circ}$  C., and cooled when coagulation has taken place. The flask is then filled to the mark with distilled water and 50 cc. of the clear solution evaporated to dryness on the water bath. The residue is dissolved in hot water and filtered into a platinum dish, again evaporated, and weighed. The peptone is then incinerated with ammonium carbonate, and the weight of ash deducted gives the weight of pure peptone. F. R. B.

**Determination of the Alkalinity of the Blood.**—J. B. Haycraft and R. J. Williamson (Chem. Cent. 1889, **2**, 615). Litmus paper made from litmus to which varying amounts of acid have been added is glazed by dipping in petroleum and then polishing. With strongly acid litmus paper only strongly alkaline blood gives a reaction. A less alkaline blood gives the reaction with less strongly reddened paper, etc. The acidity of the paper is determined by dipping into a caustic alkali solution. Cochineal, turmeric, eosine, alizarine and phenol-phtalein do not answer as well as litmus. E. H.

**Determination of Free Hydrochloric Acid in Gastric Juice.**—S. Mintz (Chem. Cent. 1889, **2**, 611). 10 cc. of the fil-

tered juice, which has been found to give a positive reaction with 2 drops of Günzberg's reagent, (2 gms. phloroglucin and 1 gm. vanillin dissolved in 28 cc. absolute alcohol) i. e., purple streaks by long heating over a small flame in a watch glass, is treated with decinormal caustic soda, in portions of  $\frac{1}{10}$  cc. at a time, until it no longer gives the reaction with Günzberg's reagent. Each tenth cc. caustic soda corresponds to 0.003646 gms. HCl. If a gastric juice contains as little as 0.036% HCl it may be detected in this way. The author has examined also the saturating power of egg albumen for free HCl. He finds that 100 cc. of a 10% solution shows an acid reaction with 2 cc. of decinormal hydrochloric acid, but Günzberg's reaction is not obtained until 15 cc. have been added. The resorcin test of Boas for free inorganic acids is less sensitive than that of Günzberg. E. H.

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## NEW BOOKS.

*Die Chemische und Mikroskopisch-bacteriologische Untersuchung des Wassers zum Gebrauche für Chemiker, Aerzte, Medicinallbeamte, Pharmaceuten, Fabrikanten und Techniker, bearbeitet von Dr. F. Tiemann und Dr. A. Gartner, Zugleich als dritte vollständig umgearbeitet und vermehrte Auflage von Kubel-Tiemann's Anleitung zur Untersuchung von Wasser. Braunschweig, Vieweg und Sohn, 1889. Seite 705, mit vielen Holzstichen und 10 Chromolithographischen Tafeln.*

Chemists who are engaged in the analysis of water are anxious for more light on the subject, and the book now before us is probably the most complete text on water analysis. It has been written with all the German fondness for detail, and the writer is often annoyed at the almost endless repetition. For instance, we are told repeatedly that in measuring out a portion of the water, it is not well to draw it up in a pipette, as it might become contaminated with saliva. It might be well to give this caution once, but when it is repeated with every method of analysis given in which small amounts of water are employed, it becomes simply ridiculous.

The work consists of two parts, the first dealing with the

chemical, and the second with the bacteriological examination of drinking water.

As we are more deeply interested in this determination of the organic matter than in any other one point connected with the chemical analysis, we will examine somewhat closely into the discussion of this subject. The permanganate process, both as given by Kubel and with its various modifications, is given a prominent place. The modification of Schulze is found to give slightly higher results than those obtained by the original method of Kubel, yet the difference is so slight, that the latter is preferred on account of its simplicity. Tidy's modification is, very properly in our estimation, condemned on account of its complexity, which leads to "a series of errors." Flack's determination with silver is found to give lower results than the permanganate process and, moreover, the former is regarded as unreliable.

The ammonium process of Wanklyn's is pronounced simple and easy of application, and is found to give fairly constant results when due care is exercised. Since it is not always easy to obtain a permanganate solution free from ammonia, a control experiment with ammonia-free distilled water is recommended. Moreover, as various organic substances yield very variable per cents of their nitrogen when treated by this method, it is not always safe to compare the results obtained from different waters. The method cannot be considered as always giving indication of the absolute amount of nitrogenous substance in the water.

The oxidation of the carbon of the non-volatile or difficultly volatile organic constituents of drinking water to carbonic acid by means of potassium bichromate and sulphuric acid according to the Wolff-Degener-Herzfeld method is found to be nearly complete. With the precautions suggested by Herzfeld, chlorides and nitrites do not materially interfere with the results. However, various organic substances contain very variable per cents of carbon. It is stated that there can be no doubt that this method gives a more reliable indication of the absolute amount of organic substances, in so far as these are not volatile in neutral solution, than that afforded by the permanganate method. This method is preferred to that of Frankland and Armstrong, which requires much time and the employment of complicated, easily broken

apparatus. The method of Dittmar & Robinson is also preferred to that of Frankland and Armstrong as simpler and as requiring less time.

Thus, it will be seen that while our authors furnish us nothing new on the vexed question of the determination of the organic matter in drinking water, they give us much useful information concerning the comparative merits of the well-known methods. This remark holds good for the whole of the chemical portion of the book. The various methods of determining the chlorides, nitrates, nitrites, hardness, etc., are discussed in great detail. The chemical portion of the work will be highly prized by the sanitary chemist.

We now turn to the bacteriological examination of drinking water. We do this with much interest, since the bacteriologist has promised to solve the whole matter and to do away with the necessity of chemical analysis. Nearly 300 pages are devoted to this part of the subject. A large portion of this is taken up with a general description of bacteria and the culture methods. The student of bacteriology will find these pages of no interest, and the one who attempts to institute himself into the mysteries of bacteriological investigation with no further information than that given here will soon find himself hopelessly confused. Another portion gives us much interesting information concerning the number of germs in water from various sources. But what are the conclusions reached by the bacteriologist in his study of the drinking water problem? They are as follows: (1) A water which contains pathogenic germs should not be used. These are words of wisdom which none will question, but our authors go on to say that the detection of pathogenic germs in drinking water is very difficult, that the non-pathogenic germs soon destroy the pathogenic varieties, and that the solution of the question of the detection of these germs in the future can hardly be expected. (2) A water into which pathogenic germs might possibly be introduced should not be used. But how are we to recognize a water into which disease-producing germs might possibly be introduced? We can do this only by knowing the source of the water and the surroundings. In other words, we can learn more by examining into the surroundings than we can

by examining the water. If this be true, why make any water analyses at all. (3) If a water be free from germs it may be used without danger of infection. (4) A large number of germs in a well whose surroundings are unfavorable should condemn the water. (5) However, if the surroundings are hygienic the presence of a large number of germs should not condemn the use of the water.

These conclusions stated by the learned authors in capital letters with due gravity appear simply ridiculous. If this is all that the bacteriologist has to teach us about water analysis we will stick to our retort.

V. C. V.

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## NOTES.

—Glatzel finds that pure manganese is formed by the action of magnesium upon a fused mixture of manganous and potassium chlorides. The metal obtained is brittle, very hard, oxidizes slowly in moist air, is easily soluble in acids, not attracted by the magnet, and has a specific gravity of 7.39 (Ber. 22, 2857).

—Mr. John Eyerman's new text-book on determinative mineralogy (short course) is in the hands of the printer, and will be issued in a few months. This work was written especially for the students in the scientific department of Lafayette College.

—Harnack has succeeded in obtaining albumen which leaves no ash when ignited. He finds that it contains no phosphorus, and is not coagulated by heat, alcohol, ether, phenol or tannin (Ber. 22, 3046).

—Dr. Chas. W. Marsh, late instructor in Chemistry in Lehigh University, has been elected Honorary University Fellow in Clark University, Worcester, Mass.

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**Obituary.**—Dr. James Prescott Joule, one of England's most illustrious scientists, died October 11, 1889, in his seventy-second year. He was a disciple of John Dalton, and his industrious researches and valuable discoveries, especially that of the mechanical equivalent of heat, entitle him to a place among the first of English physicists.

A. H. W.



—Gustave Augustin Quesneville, a French chemist. Born in Paris, January 1, 1810; died in Paris, November 14, 1889. See Jour. Soc. Chem. Ind. for November, 1889. B.

—George Hammell Cook, long professor of chemistry at Rutgers College. Born in Hanover, N. J., January 5, 1818; died in New Brunswick, N. J., Sept 22, 1889. See Eng. & Min. Jour., Oct. 5, 1889. B.

—Oscar Georg Friederich Jacobsen, Professor of Chemistry at the University of Rostock. Born in Ahrensburg Holstein, June 25; died in Rostock, Germany, August 23, 1889. B.

—Anton Geuther, Professor of Chemistry at University of Jena. Born in Neustadt, Coburg, April 23, 1833; died in Jena, August 25, 1889. B.

—August Vogel, Agricultural Chemist. Born in Munich, August 4, 1817; died in Rosenheim, August 14, 1889. B.

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THE

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# Journal of Analytical Chemistry.

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## CONVERSION OF "PARTS PER MILLION" INTO "GRAINS PER GALLON."

BY WM. P. MASON.

The necessity in many cases of reporting water analyses in "grains per gallon" renders a table, such as the following, somewhat of a convenience. The values here given are based upon a new calculation of the value of the U. S. gallon of water, in grains. In this connection it might be well to quote from an editorial note, relating to a paper published in the *American Druggist* for January, 1888. "This paper is an outcome of an inquiry set on foot by Prof. W. P. Mason, to ascertain in the first place upon what authority the *U. S. Pharmacopoeia* had based the value in grains, there given, as being equivalent to a U. S. gallon. This inquiry was addressed to the Chairman of the Committee of Revision, who replied, that so far as he was aware, there was, in reality, no *legally* defined standard of measure or relation between weight and measure in existence in this country. Until further information is supplied, the value reported by Prof. Wm. Mason deserves preference before all others. It seems, however, highly desirable that this whole question of standards and relation of weight to measure be finally settled by law, and, preliminary to this, by a new scientific investigation which might be more suitably conducted under the auspices of the National Academy of Sciences, or some other representative scientific body." The datum employed for calculating the value of the gallon is:

One cubic inch of water at 62° F., under a pressure of 30 inches of mercury, weighs, in vacuo, 252.75965 grains.

## CONVERSION TABLE.

*Conversion of "Milligrammes per Kilogramme" into "Grains per U. Gallon" of 231 Cubic Inches.*

One U. S. Gallon of Pure Water, at 60° F., weighed in air at 60° F., at Atmospheric Pressure of 30 inches of Mercury, weighs 58334.94640743 grains.

1	. . . . .	. 0.058335
2	. . . . .	. 0.116670
3	. . . . .	. 0.175005
4	. . . . .	. 0.233340
5	. . . . .	. 0.291675
6	. . . . .	. 0.350010
7	. . . . .	. 0.408344
8	. . . . .	. 0.466679
9	. . . . .	. 0.525014
10	. . . . .	. 0.583349
11	. . . . .	. 0.641684
12	. . . . .	. 0.700019
13	. . . . .	. 0.758354
14	. . . . .	. 0.816689
15	. . . . .	. 0.875024
16	. . . . .	. 0.933359
17	. . . . .	. 0.991694
18	. . . . .	. 1.050029
19	. . . . .	. 1.108364
20	. . . . .	. 1.166699
21	. . . . .	. 1.225034
22	. . . . .	. 1.283369
23	. . . . .	. 1.341704
24	. . . . .	. 1.400039
25	. . . . .	. 1.458373
26	. . . . .	. 1.516708
27	. . . . .	. 1.575043
28	. . . . .	. 1.633378
29	. . . . .	. 1.691713
30	. . . . .	. 1.750048
31	. . . . .	. 1.808383
32	. . . . .	. 1.866718
33	. . . . .	. 1.925053
34	. . . . .	. 1.983388
35	. . . . .	. 2.041723

### CONVERSION TABLE.

123

[illegible]

76 . . . . .	4.433456
77 . . . . .	4.491791
78 . . . . .	4.550126
79 . . . . .	4.608461
80 . . . . .	4.666796
81 . . . . .	4.725130
82 . . . . .	4.783465
83 . . . . .	4.841800
84 . . . . .	4.900135
85 . . . . .	4.958470
86 . . . . .	5.016805
87 . . . . .	5.075140
88 . . . . .	5.133475
89 . . . . .	5.191810
90 . . . . .	5.250145
91 . . . . .	5.308480
92 . . . . .	5.366815
93 . . . . .	5.425150
94 . . . . .	5.483485
95 . . . . .	5.541820
96 . . . . .	5.600155
97 . . . . .	5.658490
98 . . . . .	5.716825
99 . . . . .	5.775159
100 . . . . .	5.833494

## A METHOD FOR THE DETERMINATION OF IODINE IN HALOID SALTS.\*

BY F. A. GOOCH AND P. E. BROWNING.

Few problems of analysis have been more discussed than the estimation of iodine accompanying chlorine and bromine in haloid salts; and yet the constant succession of new processes is sufficiently indicative that the solution of the question is not generally regarded as satisfactorily settled. The method of Fresenius, according to which iodine is liberated by nitrous acid, collected in carbon disulphide and titrated by sodium thiosulphate, finds ready acceptance for the determination of small amounts of iodine; but when the quantity of iodine to be estimated is considerable, the

\*Amer. Jour. Sci. **39**, 188.

method is unwieldy. Probably the process most generally in use is that based upon the liberation of iodine by means of a ferric salt, and the titration of the distillate by one or other of the well-known iodometric methods. The latter method is fairly accurate, but the requirement of special apparatus for properly condensing the distillate is detrimental to rapidity and ease of execution. In this process the amount of iodine set free should be measured exactly by the reduction of the ferric salt, and were the ferrous salt produced in the course of the action sufficiently stable, the determination of its amount might be substituted for the titration of the iodine, and so the collection and further treatment of the distillate might be dispensed with ; but ferrous salts are too sensitive to atmospheric influence to preserve under the conditions of this process their own degree of oxidation, and the amount of iron found in the ferrous condition, cannot be made to serve as a trustworthy indication of the reducing action which actually takes place in the separation of the iodine. The advantage of replacing the collection and examination of the distillate by treatment of the residue is, however, so great as to constrain us to search for some substitute for the ferric salt, which, by virtue of easy reducibility may act as liberator of iodine from hydriodic acid, and, at the same time, by reason of stability after reduction, shall register accurately the quantity of iodine set free in the reducing process. The results of our experience are contained in the following account.

Strong sulphuric acid, as is well known, acts upon an iodide in a way to liberate iodine at the cost of its own loss of oxygen, though by simple dilution of the mixture thus formed the action is reversed, the iodine going back into the form of hydriodic acid, and the products of the reduction of sulphuric acid again taking back their oxygen and re-forming the acid. In the presence of any substance easily reducible by the deoxidation products of sulphuric acid the liberation of iodine, by the action of that acid upon iodides, should take place without interference, and even more easily and completely than in the absence of such a substance, while the sulphuric acid should remain at the end of the process in its original form. If the products of reduction which appear in such a case in the place of those of the sulphuric acid should be

neither readily oxidizable nor easily volatilizable, it ought to be possible to remove by heat the iodine set free in the action without disturbing the record kept by the reduced substance remaining in the residue.

The qualities of arsenic acid suggest it as a substance likely to possess just these qualities; for, though arsenious acid is converted into arsenic acid by the action of iodine in alkaline solution, in acid solution the reverse is true to at least a limited extent, and arsenic acid liberates iodine according to the equation,



In company with sulphuric acid of such strength as to liberate the iodine from hydriodic acid, the reduction should fall in the end upon the arsenic, and the arsenious oxide produced should, under proper conditions, preserve the record of the iodine liberated and removed by volatilization. We therefore undertook experimentation upon this line, and the accompanying table shows the results of a preliminary investigation of the mode of action of a mixture of sulphuric and arsenic acids upon an alkaline iodide. In making these tests a standard solution of potassium iodide was put into a test-tube, a solution of potassium arseniate was added, sulphuric acid mixed with its own volume of water was introduced, the volume of the liquid was adjusted, a film of kerosene 3 mm. thick was placed upon the surface of the liquid, and the whole was heated gently and agitated. Kerosene was chosen in preference to other solvents of iodine on account of its lightness, which makes it float upon the mixture, and its high boiling-point, which permits the application of heat to hasten and complete the reaction. Its disadvantage is the persistency with which it adheres to the walls of the test-tube, so that washing with alcohol (or other solvent) after the completion of each test is necessary to prevent the transfer of the iodine of one test to the test next succeeding. The data of these experiments are indicated in the headings.

It will be noted that in Series A, in which the absolute amount of iodine employed, its proportion to the entire volume, and the amount of the arsenic salt remained the same, the proportion of sulphuric acid being the variable element, it is shown that the proportion of sulphuric acid should reach at least twelve parts by

volume in one hundred of the solution in order that the maximum distinctness of the test may be developed. An excess of sulphuric acid beyond this proportion is not disadvantageous.

In Series B the proportion and absolute amount of iodine vary as well as the proportion of acid, while the quantity of arsenic remains invariable. The results of this series confirm those of the previous series as to the proper proportion of sulphuric acid to be used, and the sensitiveness of the test is shown to reach (in round numbers) one part by weight of iodine in six hundred thousand parts of the solution.

The tests of Series C indicate plainly that it is the sulphuric acid which is the potent agent in liberating the iodine, the experiment in which acetic acid was substituted for sulphuric acid being particularly noteworthy in this connection. The presence of arsenic acid increases the sensitiveness of the reaction, but its addition beyond a very moderate amount does not appear to be necessary or advantageous. The presence of a chloride or bromide does not impair the delicacy of the test.

The quantities of iodine taken in the experiments just described were necessarily small, and the question arises naturally as to whether the course of action would be similar in the presence of larger amounts of that substance and the correspondingly greater amount of arsenious oxide which is produced with its tendency to reverse the reaction according to which the elimination of iodine proceeds. The solution of this question was reached in the following experiments:

To 50 cm<sup>3</sup> of liquid containing 10 cm<sup>3</sup> of sulphuric acid [1 : 1], and 1 cm<sup>3</sup> of a decinormal solution of iodine in potassium iodide (0.001265 gm. of the former in 0.0018 gm. of the latter) was added 1 cm<sup>3</sup> of a decinormal solution of arsenious oxide (0.00495 gm.), an amount ten times as much as would be necessary to convert the iodine into hydriodic acid were the solution alkaline. The color of the iodine vanished gradually under the action of the arsenious acid, but was restored by the addition of 1 gm. of hydrogen potassium arseniate, and again dispelled by another portion of arsenious acid equal in amount to that introduced at first. Heat was applied at this point with the result that the color of iodine showed again faintly, and upon boiling the liquid until its



volume decreased to 25 cm<sup>3</sup> it becomes colorless and yielded no iodine when agitated with nitrous acid and chloroform.

*Series A.*

KI.	Gms. of Iodine to cm <sup>3</sup> of solution.	H <sub>2</sub> KAsO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub> [1:1]	H <sub>2</sub> SO <sub>4</sub> (strong) in 100 parts by volume	NaCl.	KBr.	Total vol.	Reaction for Iodine.
gm.		gm.	cm <sup>3</sup>		gm.	gm.	cm <sup>3</sup>	
0.0001	I:132000	I	2	10 :100	. . .	. . .	10	Faint
0.0001	I:132000	I	2	10 :100	. . .	. . .	10	Faint
0.0001	I:132000	I	2.5	12.5 :100	. . .	. . .	10	Faint
0.0001	I:132000	I	2.5	12.5 :100	. . .	. . .	10	Distinct
0.0001	I:132000	I	3	15 :100	. . .	. . .	10	Distinct
0.0001	I:132000	I	4	20 :100	. . .	. . .	10	Distinct
0.0001	I:132000	I	4.5	22.5 :100	. . .	. . .	10	Distinct
0.0001	I:132000	I	5	25 :100	. . .	I	10	Distinct

*Series B.*

0.0005	I:26400	I	2.5	12.5 :100	. . .	. . .	10	Distinct
0.000133	I:99000	I	2.5	12.5 :100	. . .	. . .	10	Distinct
0.0001	I:198000	I	3	10 :100	0.007	. . .	15	Faint
0.000067	I:198000	I	2.5	12.5 :100	. . .	. . .	10	Faint
0.000067	I:198000	I	2.5	12.5 :100	. . .	I	10	Faint
0.0001	I:198000	I	5	16.6 :100	0.005	. . .	15	Distinct
0.0001	I:198000	I	5	16.6 :100	0.005	. . .	15	Distinct
0.0001	I:264000	I	2.5	6.25 :100	. . .	. . .	20	Invisible
0.0001	I:264000	I	2.5	6.25 :100	. . .	. . .	20	Faint
0.0001	I:264000	I	5	12.5 :100	. . .	. . .	20	Faint
0.000033	I:396000	I	2.5	12.5 :100	. . .	. . .	10	Faint
0.000033	I:396000	I	2.5	12.5 :100	. . .	. . .	10	Faint
0.000033	I:594000	I	5	16.6 :100	0.005	. . .	15	Faint

*Series C.*

0.0020	I:8000	I	None. Acetic Acid 1.5 gm. (absol.)	. . .	. . .	. . .	12	Invisible
0.0010	I:13200	. . .	5 cm <sup>3</sup>	25 :100	. . .	. . .	10	Distinct
0.0002	I:66000	. . .	5	25 :100	. . .	. . .	10	Faint
0.0010	I:13200	0.2	5	25 :100	. . .	. . .	10	Marked
0.0001	I:132000	0.2	5	25 :100	. . .	. . .	10	Distinct
0.000033	I:198000	0.5	1.25	12.5 :100	. . .	. . .	5	Faint
0.000033	I:198000	0.5	1.25	12.5 :100	. . .	. . .	5	Faint
0.0001	I:264000	2.0	4	10 :100	. . .	. . .	20	Faint
0.0001	I:264000	2.0	6	15 :100	. . .	. . .	20	Faint

An experiment differing from the last in that thirty times as much arsenious oxide and iodine were taken, gave similar results. It is plain, therefore, that the arsenious acid and arsenic acid ex-

ert opposite effects under the conditions of these experiments, and that one or the other prevails according to the proportionate composition of the solution, the degree of dilution, and the temperature.

The experiments detailed in the following statement were intended to determine the conditions best adapted to eliminate the iodine from such quantities of potassium iodide as would ordinarily be dealt with in the course of analysis.

A solution of potassium iodide was placed in an Erlenmeyer beaker of 300 cm<sup>3</sup> capacity, followed by a solution of potassium arseniate and by dilute sulphuric acid [1 : 1], and the volume of the liquid was diluted to about 100 cm<sup>3</sup>. A mark was put upon the beaker to indicate the level to which the liquid was to be reduced, a spiral of platinum wire was placed in the solution to prevent explosive ebullition, and the contents of the flask were boiled until the desired degree of condensation was reached. Colorlessness of the liquid at this point, though a fair indication of the absence of free iodine, is no indication that the hydriodic acid has been completely decomposed, and so, in the event of finding the liquid colorless, it was first cooled and shaken with chloroform to prove or disprove the absence of free iodine, and then tested for the presence of hydriodic acid by shaking with nitrous acid and chloroform.

An inspection of these results shows at once that when the larger amounts of iodine are to be eliminated the proportion of sulphuric acid to the final volume after boiling needs to be increased somewhat beyond that which is necessary to set free very small portions such as were dealt with in the experiments of the earlier series.

In Series D it appears that the proportion of sulphuric acid increases from 8.3 per cent to 25 per cent of the whole volume before the liquid is found to be free from iodine as such, and even then there sometimes remain minute, though probably insignificant traces of hydriodic acid.

In the experiments of Series E the liquid was diluted after concentration and the boiling repeated, and the volatilization of the iodine was thus more nearly perfected, than in the corresponding experiments of the previous series—a proportion amounting to 16.6 per cent. apparently accomplishing the work done by 25 per cent. of the same acid in a single concentration. The results of

Series F, G, and H, are closely comparable with those of the corresponding experiments of Series D. Throughout these experiments it is again made evident that it is the proportion, and not the absolute amount, of sulphuric acid which is the great factor in the liberation of the iodine. So far as concerns the purposes of good analysis these results indicate the elimination of iodine to a reasonable sufficiency when the reduction of bulk raises the percentage by volume of the strong sulphuric acid to twenty-five, and to perfection, as in the latter determinations of Series G, when the percentage reaches twenty-eight and a half. It remains to be seen whether the arsenious oxide reduced in the separation of the iodine will resist successfully, under the conditions of these experiments, the tendency to volatilize which the presence of chlorides and bromides, and the consequent liberation of hydrochloric and hydrobromic acids, might presumably induce.

*Series D.*

KI	H <sub>2</sub> SO <sub>4</sub> [1:1]	Per cent. of strong H <sub>2</sub> SO <sub>4</sub> by volume.	H <sub>2</sub> KAsO <sub>4</sub>	Final volume.	Free Iodine.	Combined Iodine.
0.5 gm.	10 cm. <sup>3</sup>	8.3	1 gm.	60 cm <sup>3</sup>	Present	Abundant
0.5	10	10	1	50	Present	Abundant
0.5	10	12.5	2	40	Present	Distinct
0.5	10	12.5	2	40	Trace	Distinct
0.5	10	12.5	4	40	Trace	Distinct
0.5	10	16.6	1	30	Trace	. . . . .
0.5	10	16.6	2	30	Trace	. . . . .
0.5	10	16.6	2	30	Trace	. . . . .
0.5	10	16.6	4	30	None	Distinct
0.5	10	16.6	5	30	Trace	Distinct
0.5	10	25	1	20	None	Faintest trace
0.5	10	25	2	20	None	Faintest trace
0.5	10	25	2	20	None	Faintest trace
0.5	10	25	2	20	None	Faintest trace
0.5	10	25	2	20	None	Faintest trace

*Series E.*

0.5 gm.	10 cm. <sup>3</sup>	16.6	1 gm.	{ 30 cm <sup>3</sup>	None	Faintest trace
0.5	10	16.6	1	{ 30	None	Faintest trace
0.5	10	16.6	1	{ 30	None	Faintest trace
0.5	10	16.6	1	{ 30	None	Faintest trace
				{ 30		
				{ 30		

*Series F.*

0.5 gm.	15 cm. <sup>3</sup>	25	2 gm.	30 cm. <sup>3</sup>	None	Faintest trace
0.5	15	25	2	30	None	Faintest trace
0.5	15	25	4	30	None	Faintest trace

*Series G.*

0.5 gm.	20 cm. <sup>3</sup>	25	2 gm.	40 cm. <sup>3</sup>	None	Faintest trace
0.5	20	25	2	40	None	Faintest trace
0.5	20	25	2	40	None	None
0.5	20	28.6	2	35	None	None
0.5	20	28.6	2	35	None	None
0.5	20	33.3	2	30	None	None

*Series H.*

0.5 gm.	30 cm. <sup>3</sup>	25	2 gm.	60 cm. <sup>3</sup>	None	Faintest trace
0.5	30	25	2	60	None	Faintest trace

The experiments of Series I were directed to the elucidation of this point.

*Series I.*

H <sub>2</sub> SO <sub>4</sub> [1:1]	NaCl.	Final volume.	Per cent. of strong H <sub>2</sub> SO <sub>4</sub> by volume.	As <sub>2</sub> O <sub>3</sub> taken	As <sub>2</sub> O <sub>3</sub> found	Loss.
10 cm. <sup>3</sup>	1 gm.	20 cm. <sup>3</sup>	25	0.0495 gm.	0.0485 gm.	0.0010 gm.—
10	1	20	25	0.0495	0.0493	0.0002 —
10	1	20	25	0.0495	0.0488	0.0007 —
10	0.8	20	25	0.0495	0.0488	0.0007 —
10	0.5	20	25	0.0495	0.0495	0.0000 —
20	1	40	25	0.0495	0.0490	0.0005 —
20	1	40	25	0.0495	0.0490	0.0005 —
20	0.8	40	25	0.0495	0.0490	0.0005 —
20	0.5	40	25	0.0495	0.0490	0.0005 —
20	0.5	40	25	0.1385	0.1380	0.0005 —
20	1	30	33.3	0.0495	0.0476	0.0019 —
20	0.8	30	33.3	0.0495	0.0466	0.0029 —
20	0.5	30	33.3	0.0495	0.0481	0.0014 —
20	0.5	30	33.3	0.0495	0.0485	0.0010 —
20	0.5	30	33.3	0.0495	0.0490	0.0005 —
20	0.5	30	33.3	0.0495	0.0490	0.0005 —
20	0.5	30	33.3	0.0495	0.0490	0.0005 —
30	1	60	25	0.0495	0.0485	0.0010 —
30	0.8	60	25	0.0495	0.0490	0.0005 —
30	0.8	60	25	0.0495	0.0490	0.0005 —
30	0.5	60	25	0.0495	0.0490	0.0005 —

Decinormal solutions of iodine and arsenious acid were prepared, standardized, and tested against one another in the usual manner. Definite portions of the solution of arsenious acid were measured from a burette into Erlenmeyer beakers such as were used in the previous experiments, sulphuric acid [1 : 1], and sodium chloride were added, the volume of the liquid was adjusted to 100 cm<sup>3</sup>, or a little more, and the process of concentration by boiling was carried to the point desired and indicated by a mark upon the flask. After cooling, the acid was neutralized and the titration effected in the usual manner in the presence of an excess of acid potassium carbonate and starch employed as the indicator. These experiments were arranged upon the presumption that the essential conditions determining the degree of volatility of the arsenic when the reduction is effected by hydriodic acid are imitated, though neither hydriodic acid, nor arsenic acid, nor free iodine is present.

*Summary of Series I.*

H <sub>2</sub> SO <sub>4</sub> [1:1]	Final volume.	Per cent. of strong H <sub>2</sub> SO <sub>4</sub> by volume.	NaCl.	Mean loss of As <sub>2</sub> O <sub>3</sub>	No. of Determination
10 cm <sup>3</sup>	20 cm <sup>3</sup>	25	1 gm.	0.0006 gr—	3
20	40			0.0005 —	2
30	60			0.0010 —	1
10	20	25	{ 0.5 and 0.8 }	0.0003 —	2
20	40			0.0005 —	3
30	60			0.0005 —	3
20	30	33.3	{ 0.5 0.8 1.0 }	0.0008 —	5
				0.0019 —	1
				0.0029 —	1

It appears in these results that there is some loss of arsenic in nearly every case within the limits of our experimentation, the amount of volatilization increasing with the ratio of sulphuric acid to the entire volume when the quantity of chloride present is constant, and likewise with the amount of chloride when the ratio of the acid to the total liquid is constant.

The effect of increasing the amount of chloride is naturally accounted for by the "mass action" of the hydrochloric acid thus liberated upon the arsenious oxide in solution; that it is the proportion, and not the absolute amount, of sulphuric acid which

determines the degree of volatility of the arsenic is explicable upon the assumption that the smallest quantity of sulphuric acid employed is sufficient to liberate all the hydrochloric acid (or, at least, nearly all), and that this, by its action on the arsenious oxide, forms the volatile chloride proportionately to the amount of water removed bodily by concentration or withheld from effective action by the attraction of the sulphuric acid.

In extending this line of experimentation to cases involving the action of hydrobromic acid upon arsenious oxide we found it sufficient for our purpose to employ only the highest degree of concentration recorded in the previous experiments and to use 1 gm. of potassium bromide—an amount corresponding, molecule for molecule, to about 0.5 gm. of sodium chloride. The results, given in Series J, indicate that under these circumstances the loss of arsenic is inappreciable.

*Series J.*

H <sub>2</sub> SO <sub>4</sub> [1:1]	KBr.	Final volume.	Per cent. of strong H <sub>2</sub> SO <sub>4</sub> by volume.	As <sub>2</sub> O <sub>3</sub> taken.	As <sub>2</sub> O <sub>3</sub> found.	Loss.	Mean loss.
	gm.			gm.	gm.	gm.	gm.
20 cm <sup>3</sup>	I	30 cm <sup>3</sup>	33.3	0.0495	0.0490	0.0005	} 0.0001—
20	I	30	33.3	0.0495	0.0493	0.0002	
20	I	30	33.3	0.0495	0.0495	0.0000	
20	I	30	33.3	0.0495	0.0495	0.0000	
20	I	30	33.3	0.0495	0.0495	0.0000	

It appears, therefore, from the results of Series I, that, when the amount of sodium chloride present is restricted to 0.5 gm., the liquid may be boiled until the sulphuric acid amounts to 33.3 per cent. of it, with a loss, on the average, of 0.0008 gm. of arsenious oxide, and to 25 per cent. with a loss of 0.0004 gm. With either of these proportions the results are sufficiently favorable to warrant quantitative testing of a method for separating chlorine and iodine based upon the volatility of iodine and the non-volatility of arsenious oxide under the conditions. The case is even more favorable for the similar separation of bromine from iodine—the loss of arsenic amounting on the average to 0.0001 gm., under similar conditions. The experiments of Series D to H indicated that the degree of concentration at which all iodine vanishes from the liquid corresponds to the presence of

28.6 per cent. of the acid—a point midway between the points of concentration indicated above. We fixed this proportion, therefore, for the following experiments, as being rather more favorable as regards the fixity of the arsenic and perfect as to the elimination of iodine. The smallest absolute amount of sulphuric acid which we have used—10 cm<sup>3</sup> of the [1 : 1] mixture—demands evaporation of the liquid to a bulk too small to be easily determined with certainty in flasks of the shape and dimensions which we found convenient for this work. The larger amounts of acid are uncomfortably large in the subsequent neutralization. We took, therefore, 20 cm<sup>3</sup> of the [1 : 1] mixture of sulphuric acid and water as the amount best adapted to our purpose and set the limit of concentration at 35 cm<sup>3</sup>.

The potassium iodide which we used was prepared with great care, by acting with re-sublimed iodine upon iron wire, three-fourths of the iodine being added to an excess of iron covered with distilled water, decanting the solution from the excess of iron when the color of iodine had vanished, adding the remainder of the iodine, pouring the filtered solution slowly into boiling water, to which the exact amount of acid potassium carbonate necessary to combine with the iodine has been added, and filtering off the magnetic oxide of iron thus precipitated. The solution of potassium iodide thus made, very faintly alkaline and entirely free from chlorine and bromine, was made up to a suitable volume and standardized by precipitating the iodine of aliquot portions by weight as silver iodide, which was heated and weighed upon asbestos. Weighed portions of this solution, containing approximately 0.5 gm. of potassium iodide to 30 cm<sup>3</sup>, were taken for the tests in which the larger quantities of iodine were introduced; measured portions of a solution made by diluting the former were employed in the tests involving the smaller amounts.

The sodium chloride and potassium bromide used were shown to be free from iodine, and the hydrogen potassium arseniate contained no arsenious acid.

The mode of proceeding was, in general, like that of the previous experiments. The solution of potassium iodide was put in an Erlenmeyer beaker of 300 cm<sup>3</sup> capacity, 2 gms. of hydrogen potassium arseniate were added in solution and followed by 20 cm<sup>3</sup>

of sulphuric acid [1 : 1], the liquid was diluted with water to a little more than 100 cm<sup>3</sup>, a platinum spiral was placed in the flask to secure quiet ebullition, a trap made by cutting off a two-bulb drying tube about an inch from the inside bulb was hung, large end downward, in the mouth of the flask to prevent mechanical loss, and the liquid was boiled until the level reached the 35 cm<sup>3</sup> mark upon the flask. At this point the flask was cooled, the acid nearly neutralized with sodium hydrate in solution, the neutralization completed by acid potassium carbonate, 20 cm<sup>3</sup> of the last being added in excess, a definite portion of starch indicator added, and the contents in arsenious acid determined by titration with a decinormal solution of iodine for the larger amounts, and a centinormal solution for the smaller. Due correction was made for the amount of iodine necessary to develop the test-color in a solution prepared and treated similarly in all respects to the experimental solutions excepting the introduction of the iodine—the correction amounting to a single drop more of the decinormal solution than was required to produce the end reaction in the same volume of pure water containing only the starch indicator.

The decinormal solution of iodine was made by dissolving 12.65 gms. of carefully resublimed iodine in potassium iodide (proved free from iodate) and diluting to a liter. The centinormal solution was made by diluting the stronger solution. The standardizing was effected by comparison with a solution of arsenious oxide containing 4.95 gms. to the liter. This mode of fixing the value of the solution should, and, as the sequel proved, did indicate the correct standard, but for the sake of confirmation the value of the arsenic solution was redetermined by titration against iodine specially purified by subliming off potassium iodide, re-subliming between watch-glasses, and exposing during forty-eight hours over sulphuric acid. Portions of the iodine thus prepared were weighed in a glass-stoppered weighing bottle, dissolved in the same without danger of volatilization by introducing pure solid potassium iodide and a little water, and diluted and treated with the solution of arsenious acid measured from a burette until the color of iodine vanished. The excess of arsenious oxide was determined by titrating against the standard solution of iodine whose value



in terms of measured portions of the solution of arsenious oxide was perfectly known.

In series K are detailed experiments which follow the line marked out for the separation of iodine from chlorine and bromine in the haloid salts, excepting that the iodide was entirely omitted for the purpose of discovering whether hydrochloric and hydrobromic acids possess reducing action upon arsenic acid under the conditions. The evidence is plain that no arsenious oxide is formed by the action of 0.5 gm. of sodium chloride upon 2 gm. of the arseniate under the circumstances as given.

Hydrobromic acid, on the contrary, is slightly decomposed with the evolution of bromine enough to give visible color to the concentrated liquid, but the amount of bromine lost, as indicated by the arsenious acid produced in its evolution, is only 0.0003 gm. for 0.1 gm. of the bromide. Further experiments indicated, however, that concentration cannot go on to a volume less than 35 cm<sup>3</sup> without causing serious loss when the maximum amount of bromide is present.

*Series K.*

H <sub>2</sub> SO <sub>4</sub> [1:1]	H <sub>2</sub> KAsO <sub>4</sub>	NaCl.	KBr.	Final volume.	Iodine corres- ponding to As <sub>2</sub> O <sub>3</sub> reduced.	Chlorine corres- ponding (avr.)	Bromine corresp'ng (average)
					gm.	gm.	gm.
20 cm <sup>3</sup>	2 gm.	0.5 gm.	. .	35 cm <sup>3</sup>	0.0000	0.0000	. . .
20	2	0.5	. .	35	0.0000		
20	2	0.5	. .	35	0.0000		
20	2	. .	0.1 gm.	35	0.0003	. . .	0.0001
20	2	. .	0.1	35	0.0001		
20	2	. .	0.1	35	0.0001		
20	2	. .	0.5	35	0.0005	. . .	0.0003
20	2	. .	0.5	35	0.0005		
20	2	. .	0.5	35	0.0005		

In Series L are given the results of twenty-six determinations of iodine by the method outlined.

Upon inspection of these results it appears that the method is good and reliable under all the conditions tested.

When neither chloride nor bromide is present, the iodine is determined with a mean error of 0.0002 gm.

When sodium chloride accompanies the iodine, the results show a loss of arsenious oxide and a consequent apparent deficiency of iodine—as we should expect in accordance with indications of

Series I. This deficiency proves to be proportional to the amount of iodide broken up, or the arsenious oxide thus produced. For 0.56 gm., approximately, of potassium iodide and 0.5 gm. of sodium chloride the deficiency measured in iodine amounted to 0.0011 gm. When the potassium iodide is decreased ten-fold (or more) the deficiency falls to 0.0002 gm. It should be recalled, too, in this connection that the results of Series I pointed to increasing volatility of the arsenic with the increase of the sodium chloride present.

*Series L.*

No.	H <sub>2</sub> SO <sub>4</sub> [1:1]	K <sub>2</sub> KAsO <sub>4</sub>	NaCl.	KBr.	Final volume	KI taken.	Theory for Iodine.	Iodine found.	Error.	Average Error.
		gm.				gm.	gm.	gm.	gm.	gm.
(1)	20cm <sup>3</sup>	2	. .	. .	35cm <sup>3</sup>	0.5616	0.4080	0.4079	0.0001—	0.0002—
(2)	20	2	. .	. .	35	0.5630	0.4091	0.4086	0.0005—	
(3)	20	2	. .	. .	35	0.5622	0.4083	0.4086	0.0003+	
(4)	20	2	. .	. .	35	0.0506	0.0400	0.0396	0.0004—	
(5)	20	2	. .	. .	35	0.0506	0.0400	0.0391	0.0009—	
(6)	20	2	. .	. .	35	0.0506	0.0400	0.0400	0.0000	
(7)	20	2	. .	. .	35	0.0506	0.0400	0.0401	0.0001+	
(8)	20	2	. .	. .	35	0.0051	0.0040	0.0037	0.0003—	
(9)	20	2	. .	. .	35	0.0051	0.0040	0.0038	0.0002—	0.0011—
(10)	20	2	0.5	. .	35	0.5611	0.4077	0.4066	0.0011—	
(11)	20	2	0.5	. .	35	0.5619	0.4082	0.4073	0.0009—	
(12)	20	2	0.5	. .	35	0.5624	0.4086	0.4073	0.0013—	
(13)	20	2	0.5	. .	35	0.0506	0.0400	0.0402	0.0002+	0.0002—
(14)	20	2	0.5	. .	35	0.0506	0.0400	0.0395	0.0005—	
(15)	20	2	0.5	. .	35	0.0051	0.0040	0.0037	0.0003—	
(16)	20	2	0.5	. .	35	0.0051	0.0040	0.0037	0.0003—	
(17)	20	2	. .	0.5	35	0.5619	0.4082	0.4092	0.0010+	0.0008+
(18)	20	2	. .	0.5	35	0.5697	0.4138	0.4136	0.0002—	
(19)	20	2	. .	0.5	35	0.5622	0.4083	0.4099	0.0016+	
(20)	20	2	. .	0.5	35	0.0506	0.0400	0.0410	0.0010+	
(21)	20	2	. .	0.5	35	0.0506	0.0400	0.0404	0.0004+	0.0008+
(22)	20	2	. .	0.5	35	0.0051	0.0040	0.0048	0.0008+	
(23)	20	2	. .	0.5	35	0.0051	7.0040	0.0049	0.0009+	
(24)	20	2	0.5	0.5	35	0.5626	0.4087	0.4083	0.0004—	
(25)	20	2	0.5	0.5	35	0.5660	0.4112	0.4111	0.0001—	0.0003—
(26)	20	2	0.5	0.5	35	0.5622	0.4083	0.4079	0.0004—	

The presence of potassium bromide results in the liberation of minute amounts of bromine and a consequent increase in the arsenious oxide and apparent excess of iodine. The mean error due to this cause is 0.0008 gm. for 0.5 gm. of the bromide, and the variation in the quantity of iodide present is without effect upon it.

The simultaneous action of the chloride and bromide tends, of course, to neutralize the error due to each. Thus, in the mixture

weighing about 1.5 gm. and consisting of sodium chloride, potassium bromide, and potassium iodide in equal parts, the mean error amounts to 0.0003 gm.—. The largest error in the series is 0.0016 gm.+, when the bromide was at its maximum and no chloride was present; and the next largest was 0.0013 gm.—when the chloride was at its maximum and no bromide was present.

It is obvious that when the amounts of chloride and bromide present are known approximately it is possible to apply corrections which shall eliminate errors in the indicated amount of iodine due to the action of these substances. From the averages of Series L it is apparent that the amount to be added in each case may be obtained by multiplying the product of the weights in gms. sodium chloride and potassium iodide by the constant 0.004; and the amount to be subtracted, by multiplying the weight in gms. of potassium bromide by 0.0016. Thus, for example, the correction in (24) will be 0.0011 gm.+ ( $=0.5 \times 0.56 \times 0.004$ ) and 0.0008 gm.— ( $=0.5 \times 0.0016$ ). The individual results of Series L, thus corrected will stand as follows:

No. of Exp.	Theory for Iodine.	Corrected amount of Iodine found.	Error.	Mean error.
(1)	0.4080 gm.	0.4079 gm.	0.0001 gm.—	} 0.00001 gm.—
(2)	0.4091	0.4086	0.0005 —	
(3)	0.4083	0.4086	0.0003 +	
(4)	0.0400	0.0396	0.0004 —	
(5)	0.0400	0.0391	0.0009 —	
(6)	0.0400	0.0400	0.0000	
(7)	0.0400	0.0401	0.0001 +	
(8)	0.0040	0.0037	0.0003 —	
(9)	0.0040	0.0038	0.0002 —	
(10)	0.4077	0.4077	0.0000	
(11)	0.4082	0.4084	0.0002 +	
(12)	0.4086	0.4084	0.0002 —	
(13)	0.0400	0.0403	0.0003 +	
(14)	0.0400	0.0396	0.0004 —	
(15)	0.0040	0.0037	0.0003 —	
(16)	0.0040	0.0037	0.0003 —	
(17)	0.4082	0.4084	0.0002 +	
(18)	0.4138	0.4128	0.0010 —	
(19)	0.4083	0.4191	0.0008 +	
(20)	0.0400	0.0402	0.0002 +	
(21)	0.0400	0.0396	0.0004 —	
(22)	0.0040	0.0040	0.0000	
(23)	0.0040	0.0041	0.0001 +	
(24)	0.4087	0.4086	0.0001 —	
(25)	0.4112	0.4114	0.0002 +	
(26)	0.4083	0.4082	0.0001 —	

The mode of proceeding in the analysis of a mixture of alkaline chlorides, bromides and iodides, according to this method may be briefly summarized as follows:

The substance (which should not contain of chloride more than an amount corresponding to 0.5 gm. of sodium chloride, nor of bromide more than corresponds to 0.5 gm. of potassium bromide, nor of iodide much more than the equivalent of 0.5 gm. of potassium iodide) is dissolved in water in an Erlenmeyer beaker of 300 cm<sup>3</sup> capacity, and to the solution are added 2 gms. of dihydrogen potassium arseniate dissolved in water, 20 cm<sup>3</sup> of a mixture of sulphuric acid and water in equal volumes, and enough water to increase the total volume to 100 cm<sup>3</sup>, or a little more. A platinum spiral is introduced, a trap made of a straight two-bulb drying-tube cut off short is hung with the larger end downward in the neck of the flask, and the liquid is boiled until the level reaches the mark put upon the flask to indicate a volume of 35 cm<sup>3</sup>. Great care should be taken not to press the concentration beyond this point on account of the double danger of losing arsenious chloride and setting up reduction of the arseniate by the bromide. On the other hand, though 35 cm<sup>3</sup> is the ideal volume to be attained, failure to concentrate below 40 cm<sup>3</sup> introduces no appreciable error. The liquid remaining is cooled and nearly neutralized by sodium hydrate (ammonia is not equally good), neutralization is completed by hydrogen potassium carbonate, an excess of 20 cm<sup>3</sup> of the saturated solution of the latter is added, and the arsenious oxide in solution is titrated by standard iodine in the presence of starch.

With ordinary care the method is rapid, reliable and easily executed, and the error is small. In analyses requiring extreme accuracy all but accidental errors may be eliminated from the results by applying the corrections indicated.

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### A NEW PROCESS FOR THE SURE DETECTION OF SUGAR IN URINE.

By H. A. BISHOP.

The detection of sugar in the urine by the present methods is difficult. The chemical analysis of the urine, I believe, should be conducted with the same judgment as the chemical analysis of

any other fluid. First, we must examine the external properties—the color, gravity, odor, and reaction. While neither of these can furnish positive proof of the absence of certain constituents, they sometimes give indications of value. The fermentation test does not in all cases seem reliable; for urine passed after taking phenol contains bodies such as phenyl-sulphates and cresyl-sulphates. Salicylic and salicyluric acids occur in the urine after the administration of the former. Phenol and salicylic acid may be recognized after the administration of salol. Arsenic is absorbed into the system after its administration, and is found in the urine. There is proof that mercurials are absorbed and eliminated by the urine, as is also true of iodides, sulphur, etc. As fermentation is arrested by substances of antiseptic properties, it would seem impossible for complete fermentation to take place in a fluid in which such substances exist. The same conditions would also interfere with Fehling's test; for Fehling's solution is reduced in presence of arsenic, salicylic acid, and other organic substances liable to be present. The bismuth test would probably fail in presence of sulphur, and sulphur invariably is present either in the free or combined state. It is therefore absolutely necessary that the fluid be as free as possible from such bodies as would interfere with the tests. The following method will, it is believed, serve for the determination of sugar in the urine.

The urine is first shaken with animal charcoal. As soon as the fluid appears colorless, add baryta water, boil, allow to cool, and filter. To the filtrate add cautiously a weak solution of cupric sulphate ( $\text{CuSO}_4$ ) in moderate excess, allow to stand for one hour in a covered vessel, decant and filter. To the clear solution add  $\text{H}_2\text{S}$  water in excess, or better, transmit  $\text{H}_2\text{S}$  gas through the solution. Then filter, apply a gentle heat to expel the  $\text{H}_2\text{S}$  which may be present, and again filter. The solution is now practically free from everything which would interfere with the determination of sugar, and the operation may be finished by either of the usual methods.

For the test analyses I took 125 cc. of normal urine free from sugar, in which I dissolved  $2\frac{1}{2}$  gms. inverted sugar, together with phenol, salicylic acid, arsenic, and mercuric iodide. From the above it will be seen that in 1 cc. there will be 0.05

gram of sugar ; 31.25 cc. treated by the fermentation test gives 6.26 per cent. glucose. 31.25 cc. titrated by Fehling's solution gives 12.34 per cent glucose. The remaining 62.5 cc. first treated by the process mentioned gave the following :

31.25 cc. by fermentation test, 8.98 per cent. glucose.

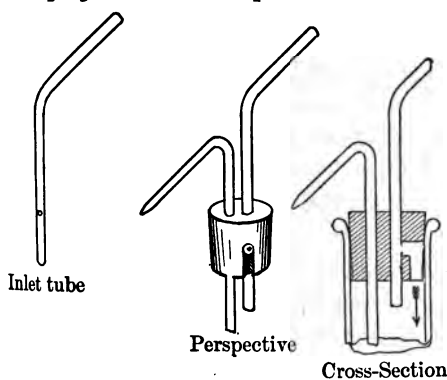
31.25 cc. by Fehling's solution, 9.02 per cent. glucose.

### A NEW VALVE FOR WASH BOTTLES.

BY DAVID H. BROWNE.

In view of the fact that metallurgical and technical chemists have daily occasion to use hot acids, ammonia, and other fuming liquids in the washing of precipitates, a wash bottle which will automatically throw a prolonged stream of liquid, and retain all disagreeable fumes, will be appreciated by the fraternity. A strong objection to the use of a rubber bulb, attached to the wash bottle, is the fact that a slight rise in the temperature of the room will force the liquid out of the bottle ; while the ordinary rubber valve as described by Blair in "The Analysis of Iron," will swell and become useless in a short time when exposed to the fumes of hot acids. A very simple apparatus can be made in a few minutes which obviates both these difficulties.

A rubber stopper, doubly perforated, and of such size that it will project about a quarter inch above the neck of the wash



bottle, is chosen, a lead pencil or penholder passed into one of the holes, and a small hole drilled through the side of the stopper till the borer meets the wooden plug. A wedge-shaped channel is then cut in the side of the stopper from this side hole to the lower end of the cork. A piece of glass

tubing is now closed at one end and a small opening about the size of a pin's head made in the glass an inch from the closed end. This can be easily done by a small flame directed upon

the surface of the glass, while air is blown into the tube. This small opening is made level with the rest of the tube, and the glass is bent at the regulation angle, about two inches above this opening. This is then placed in the rubber stopper, so that the hole in the glass tube and that cut in the stopper will coincide. An exit tube for the escape of the liquid is made as usual, and the tubes and stopper placed in the neck of the wash bottle in such a way that, when air is blown in, it passes through the side hole in the stopper, down the wedge-shaped groove, and forces the liquid up the exit tube. A very slight rotation of the inlet tube, after the liquid has begun to flow, will close the valve, and the pressure of the enclosed air will maintain the stream, which can instantly be stopped by reversing the rotation. If the apparatus is well made the angle of rotation of the inlet tube is very slight, not over twenty degrees.

I have had this apparatus in use for several months, and find that it does not get out of order, is much easier to handle, and saves more labor in the washing of precipitates than any other form of wash bottle. The inlet tube is so small that no appreciable evaporation of ammonia occurs, nor does a rise in the temperature of the laboratory result in an undesirable washing of the working benches.

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### THE SANITARY EXAMINATION OF WATER AS PRACTICED IN THE HYGIENIC LABORATORY OF THE UNIVERSITY OF MICHIGAN.

By V. C. VAUGHAN.

When the Legislature of Michigan made an appropriation for the building and equipment of a laboratory of hygiene in the University, the purposes of the laboratory were stated in order of importance as follows :

- (1.) Original research concerning the causation of disease.
- (2.) The sanitary examination of samples of food and drink at the request of health officers in the State.\*
- (3.) The instruction of students in the various branches of hygiene.

To the second of these objects, the health officers of the State

\*The fees charged for this work go into the laboratory fund.

have not been slow to respond. The laboratory has been in operation now but little more than a year. During that time we have been called upon to report on the fitness or unfitness for potable purposes of more than one hundred samples of water. All, with the exception of fifteen of these, which have been sent from other States, have been furnished by health officers or village authorities within the State.

We have been very anxious to make these reports upon the potability of the water as thorough and as satisfactory as possible. Our experience has led us to the following conclusions concerning methods of examination :

(1.) The report must be made to the health officer within a week, at most. Typhoid fever appears in a village. The doctor at once suspects the drinking water. He naturally weighs the evidence before him, and comes to some conclusion, right or wrong, in case there are several sources from which the sick may have obtained the poison, as to the exact water, which is at fault. There are always those who disagree with the doctor, or, as is likely to be the case, a rival physician has as many cases, and he is equally certain that some other water is the cause of the trouble ; and there are still in the land, physicians who believe that the poison of typhoid fever does not enter the system with the drinking water, and that the disease is due to certain meteorological or other equally undefined conditions. Each side has its partisans, and much bad blood not infrequently makes itself manifest. The health officer sends to the laboratory one or more samples of water, and the report is anxiously looked for. We therefore regard all methods of water analysis, which require more than a week at most before the health officer receives his return as not suitable for our purposes. For this reason we have been compelled to give up the idea, with which we started out, of identifying positively and certainly all the germs which might be present in the water, before reporting to the health officer.

(2.) If the water is bad, the fact should be so plainly and forcibly set forth in the report that no reasonable person can question it. It can hardly be expected that a chemical analysis alone will do this.

(3.) The reports should be made in such a manner that they



will be scientifically as well as practically of value. After several years of such work we hope to have a mass of evidence in these reports, which may furnish us with the key to certain problems which to-day cannot be solved.

(4) When the report is made, the work with that sample of water should be left in such a condition that for strictly scientific purposes it can be continued.

Our general method of procedure is as follows :

If a health officer, or other person has signified his intention of sending a sample of water, we express to him a one gallon sterilized glass stoppered bottle surrounded by a light wooden frame. This is filled with the water and returned. As soon as it reaches the laboratory, gelatine plates are made, and a tube of sterilized beef-tea is inoculated with one drop of the water. The plates are kept at the ordinary temperature of the room and the germs developed on these are counted after 24, 48 and 72 hours. The tube of beef-tea is placed in an incubator and kept at 38° C. for 24 hours, after which an animal is inoculated. In the great majority of cases, if there are poison-producing germs present, the animal dies within 12 hours. The post-mortem is made and plates inoculated from the liver, spleen, kidney, and sometimes other organs. Within 36 hours more the germs on these plates have developed. In the meantime the chemical and microscopical examinations have been made, and 72 hours after the water has been received, the report is complete.

The morphology, the physiology, and the chemistry of the microorganisms can then be worked out at leisure.

The following is a copy of the blank used for making the report :

*Report of the Sanitary Examination of Water sent by.....*

*Source of the Water, with remarks on the sanitary surroundings,*

#### PHYSICAL PROPERTIES.

*Color .....*

Odor .....

Reaction .....

Hardness .....

#### CHEMICAL ANALYSIS.

##### PARTS PER MILLION.

- (1) *Total residue obtained by evaporation at 110° C.*.....
- (2) *Residue after ignition, or inorganic matter in residue*.....
- (3) *Organic residue, or loss on ignition*.....
- (4) *Amount of earthy bases, calculated as oxides*.....
- (5) *Amount of chlorine, calculated as sodium chloride*.....
- (6) *Amount of sulphates calculated as  $SO_3$* .....
- (7) *Parts of Potassium Permanganate reduced by the organic matter in the water*.....
- (8) *Amount of free ammonia*.....
- (9) *Amount of albuminoid ammonia*.....
- (10) *Amount of nitrates, calculated as  $N_2O_5$* .....
- (11) *Amount of nitrites, calculated as  $N_2O_3$* .....

##### EXPLANATION.

While no absolute standard for the chemical purity of drinking water can be given, the following conclusions may be regarded as approximately correct :

- (1) The total residue should not exceed 500 parts per million.
- (2) The inorganic residue may constitute the total residue.
- (3) The smaller the amount of organic residue the better the water.
- (4) The amount of earthy bases should not exceed 200 parts per million.
- (5) The amount of sodium chloride should not exceed 10 parts per million.  
A larger amount may be expected, however, in certain salt-producing districts.
- (6) The amount of sulphates should not exceed 100 parts per million.
- (7) The organic matter in one million parts of the water should not reduce more than 8 parts of potassium permanganate.
- (8) The amount of free ammonia should not exceed 0.05 part per million.
- (9) The amount of albumoid ammonia should not exceed 0.15 part per million.

- (10) The amount of nitric acid should not exceed 0.5 part per million.
- (11) The best waters contain no nitrous acid, and any water which contains this substance in quantity sufficient to be estimated, should not be regarded as a safe drinking water.

NOTE.—The word "trace," whenever used, indicates the existence of the substance in quantity sufficient to be recognized by the test, but too small to be determined quantitatively.

#### MICROSCOPICAL EXAMINATION.

*Description of deposit, if any, magnified 100 diameters.....*

*Same magnified 500 diameters.....*

#### EXPLANATION.

Six ounces of the water are placed in a conical glass, and the deposit, if any, is examined after from 12 to 24 hours. The presence of any appreciable deposit, especially if it be of animal or vegetable nature, would detract from the suitability of the water.

#### BACTERIOLOGICAL EXAMINATION.

Number of germs developed on a gelatine plate inoculated with one drop of water :

(1) *After 24 hours.....*

(2) *After 48 hours.....*

(3) *After 72 hours.....*

Remarks on the kinds of germs observed :

.....

#### INOCULATION EXPERIMENTS.

*Kind of animal inoculated with the germs.....*

*Method of inoculation.....*

*Kind, amount and age of culture used.....*

*Results of the inoculation.....*

*Post-mortem appearances.....*

*Description of the germs, if any, found in the organs.....*

*In what organs were the germs, if any, found growing.....*

#### EXPLANATION.

One drop of the water is added to one drachm of some culture medium,

such as beef tea, and this after it has been kept at the temperature of the body for 24 hours or longer is used for inoculating animals.

## CONCLUSIONS.

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Director of the Michigan State Laboratory of Hygiene.

*Ann Arbor*, ..... 189

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY.  
COMMUNICATED BY PROF. W. E. STONE.]

## I. THE ANALYSIS OF SOAPS.

BY J. F. SCHNAIBLE.

Our knowledge of the composition of soaps and of successful methods of examining the same does not seem commensurate with the importance of the subject. The nature of soap makes its adulteration possible to an extent which greatly decreases its value, or even in such ways that it becomes positively injurious. Again, a very inferior article may be made without such intention by a careless or ignorant manufacturer, but these variations of composition are not generally apparent to the ordinary consumer.

Theoretically, a soap should contain only the combining equivalents of alkalis and fatty acids associated with a small percentage of water. In soap which has not been carefully made, however, there may easily exist more or less unsaponified fat or free alkali, as the case may be. Besides these variations, the commercial soap often contains varying amounts of resin, alkaline carbonates and silicates, borax, glauber's salt, pearl ash, salt, starch, silex, talc, sand, etc., complicating the analysis to a corresponding degree. In toilet soaps we may find glycerine, alcohol, sugar, coloring matter, etc., while medicated soaps will often contain phenol, sulphur, potassium iodide, and other medicinal substances.

Of the many analytical methods proposed, few are quite satis-

factory. After a careful comparison, I have found the following to give very acceptable results :

#### WATER.

For the determination of water, the method of Loewe\* was employed with good results. From 8-10 gms. of the soap (which has been reduced to very fine shavings, and represents an average sample) is weighed out between watch glasses and heated in the air-bath, at first from 60°-70° C., to avoid melting, then at 100°-105° C., to constant weight. In selecting the sample in this, as well as in all subsequent determinations, it is essential that an average specimen be obtained, since the content of water in the different parts of the bar varies considerably.

This is best effected by cutting away about one-third from the end and evenly scraping the cut surface of the remainder until a sufficient amount is obtained for the analysis.

If the determination of free alkali is of considerable importance, the soap should be dried in an atmosphere free from CO<sub>2</sub>. The loss at 105° C. represents the water together with other volatile constituents, such as alcohol and essential oils, which may be present.

#### UNSAAPONIFIED MATTER.

For the determination of unsaponified matter,† the soap, which has been dried in the manner indicated, is extracted in a Soxhlet extraction apparatus with petroleum ether, which, for this purpose should boil below 80° C. and should leave no residue on evaporation. After the extraction is complete, the petroleum ether is distilled off, the residue dried at 100° C. and weighed.

In a boiled, well-made laundry soap, there should be no unsaponified matter unless the same has been subsequently added. In addition to unsaponified fats, foreign matters are sometimes found in the petroleum ether extract, such as a soft paraffin (so-called "Mineral Soap Stock"), waxes, hydrocarbon oils, phenol, etc. If waxes are found to be present, the dried soap should be extracted with boiling toluene, which dissolves the same better than petroleum ether.

#### TOTAL ALKALI. FATTY ACIDS.

The dried soap thus freed from unsaponified matter is next dis-

\*Fresenius Zeitschr. XIX, p. 112.

†Allen's Com. Org. Analysis, Vol. II.

solved in hot water, preparatory to determining the total alkali and fatty acids.

A pure soap dissolves completely in hot water, and no ordinary product should leave more than a slight residue. If the article examined is a "scouring soap," the insoluble residue will be found to contain large quantities of fine sand, and sometimes talc.

The residue, if appreciable, should be washed by decantation, and eventually brought upon a filter with hot water, dried at 100° C., and weighed, after which, if desired, it can be subjected to further examination.

To the aqueous solution is added an excess of  $\frac{n}{2}\text{H}_2\text{SO}_4$ , setting free the fatty acids which rise to the surface. The beaker or vessel in which the precipitation was effected is next cooled with ice water. When the fatty acids\* have solidified, it is best to decant the liquid, remelt with hot water two or three times to remove any enclosed mineral acid, again cool, filter, and wash with cold water until the washings are no longer acid, as shown by litmus.

The filtrate from the insoluble fatty acids contains the total alkali now present as sulphate, the excess of sulphuric acid and any glycerine which may have been present in the soap, if saponification was effected in the cold. The acid liquid may further contain a small amount of soluble fatty acids. It is first titrated with  $\frac{n}{2}\text{KOH}$ , using methyl orange as †indicator. From the original amount of  $\text{H}_2\text{SO}_4$  added and the number of cc.  $\frac{n}{2}\text{KOH}$  required to neutralize the excess of the same, can be determined the total alkali of the sample. It is calculated to  $\text{Na}_2\text{O}$ .

After the liquid has been rendered neutral to methyl orange (which indicates the mineral acid), phenol-phthalein is added and more  $\text{KOH}$  is run in. The number of cc. of  $\text{KOH}$  required for neutralizing to phenol-phthalein corresponds to soluble fatty acids, and is calculated to caprylic anhydride ( $\frac{\text{C}_7\text{H}_{15}\text{CO}}{\text{C}_7\text{H}_{15}\text{CO}}\text{O}$ ) in the absence of more definite knowledge as to their nature.

The solution is now concentrated and tested for glycerine, which may be determined by evaporating to dryness and extracting with ether-alcohol mixture, ‡or else by oxidizing to oxalic acid by means of permanganate§ (not always applicable||).

\*Bulletin No. 13, St. 4, p. 456, U. S. Dept. Agr. Chem. Div.

†Allen's Com. Org. Analysis, Vol. II, p. 260.

‡Chem. Zeit. 8, 1667.

§Chem. Zeit. 9, 975.

||Allen. Com. Org. Analysis, Vol. II, p. 290.

In soaps containing silicates of the alkalies (a not unusual constituent), the gelatinous silicic acid which separates on the addition of  $\text{H}_2\text{SO}_4$ , remains with the fatty acids on filtration. To separate the fatty acids from this, as well as all other impurities which may be present, I have found the following method effective.

The funnel containing the filter with the fatty acids is placed in a small beaker and heated in an air-bath (Allen's method). As the filter dries, the fatty acids pass through it and collect in the beaker below, while all impurities (silicic acid, traces of silica, talc, etc.) remain behind on the filter. Of course it is necessary to wash the filter, which remains saturated with the fatty acids, with hot redistilled alcohol or petroleum ether, or else exhaust in an extraction apparatus. The alcohol or petroleum ether is distilled off and the residue treated in the same way as the main quantity of fatty acids.

In determining the fatty acids in a soap, it is frequently convenient to extract with ether in a separatory funnel.\* To do this the soap solution is placed in the funnel and shaken with  $\text{H}_2\text{SO}_4$  and ether. The separated acids are at once dissolved in the ether. The aqueous solution may be drawn off below, the ethereal solution washed with water, the ether evaporated, and the residue dried at  $100^\circ \text{C}$ . and weighed.

Some analysts recommend† melting the fatty acids (if soft) with a weighed amount of paraffin or stearic acid, as by this means a firm coherent cake is obtained, which can easily be handled. The cake is washed, dried and weighed, and the weight of paraffin deducted.

This method, however, is not applicable when it is desired to make a further examination of the fatty acids, to determine their origin; in this case it is better to extract with ether, as given. Since the fatty acids exist in the soap as anhydrides, and are weighed as hydrates, it is necessary to multiply the weight found by the factor .97, which gives the weight of fatty anhydrides.

The fatty acids, after having been weighed, may be titrated with  $\frac{n}{2} \text{KOH}$ , and from these data may be ascertained what por-

\*Chem. News 43, 218.

†Chem. News 43, 67.

tion of the total alkali exists in combination with the acid as soap.

#### FREE ALKALI.

To determine the per cent. of free alkali\* in soap, a separate portion is weighed out and extracted with *neutral* alcohol in an extraction apparatus. The caustic alkali is determined in the alcoholic solution by titrating with  $\frac{n}{2}$  HCl, using phenol-phthalein as indicator.

If, however, the soap contains unsaponified fat, as is frequently the case if made by the so-called "cold process," this method cannot be used, since in alcoholic solution unsaponified fat would be readily saponified by the free caustic alkali present.

In such a case the soap must first be dried in an atmosphere free from CO<sub>2</sub> at 100° C., the unsaponified matter extracted with petroleum ether, and finally the soap dissolved in alcohol and the free alkali determined in the alcoholic solution as before.

The carbonate of soda, silicate of soda, borax, and everything insoluble in alcohol, remains behind in the extraction tube, and may be dried at 100° C. and weighed. If considerable, it may be further treated, as follows :

First, it should be exhausted with boiling water. One-half of this solution is then titrated with  $\frac{n}{2}$  HCl, using methyl orange as indicator. The amount of acid required corresponds to carbonate, silicate and borate. In this solution sulphates may also be determined and starch and gelatine tested for.

The other half of the solution is examined qualitatively for carbonate, silicate and borate. If there remains considerable residue insoluble in water, it may be dried at 100° C., weighed, and further examined.

#### RESIN.

Resin is a very common constituent of soaps, the resinsates of alkalies having a similar action to soaps, and the cheapness of the material often suggesting a partial substitution of it for the natural fats and oils.

As a qualitative test for resin. Gottlieb's† method is reliable and easily made.

\*Allen. Com. Org. Analysis, Vol. II, p. 251.

†Benedikt, Analyse der Fette u. Wachsarten, p. 121.



The soap is dissolved in water and heated to boiling. A strong solution of  $\text{MgSO}_4$  is added until the fatty acids are completely precipitated. The magnesium resinates remain in solution. After boiling 2-3 minutes, the solution is filtered and the hot filtrate acidified with  $\text{H}_2\text{SO}_4$ . In the presence of resin the liquid becomes turbid, due to the separated resin acids. The boiling should be continued for one-half hour, to make sure that the turbidity is due to the resin acids and not to volatile fatty acids.

Barford\* recommends as a qualitative test for resin to dissolve the soap or mixed fatty and resin acids in 80 per cent. alcohol, and add an excess of an alcoholic solution of  $\text{CaCl}_2$  with ammonia to alkaline reaction. After cooling, the precipitate is washed and filtered. The filtrate contains the calcium salt of the resin acids, together with a slight amount of calcium oleate. If it is now acidified with  $\text{HCl}$ , the resin separates as a soft, gummy and viscous mass.

For the quantitative determination of resin, several processes have been recommended.

Gladding's method,† which is based on the solubility of the silver resinates in ether, is open to objection on account of the inaccuracy arising from the repeated transfers of the ethereal solution and the numerous readings to be taken, and also on account of the evaporation of the ether which takes place.

Furthermore, Wright and Thompson have shown the correction for oleic acid, which Gladding introduces to be not at all constant.

A very convenient method, and one which I have found to give good results, is that proposed by V. Hübl and Stadler.‡

.5-1 gm. of the mixture of fatty and resin acids is heated in a closed flask on the water-bath with about 20 cc. alcohol to complete solution. The acids are neutralized with alkali, using phenol-phthalein as indicator. The alcoholic soap solution is then poured into a beaker, the flask rinsed with water, the solution diluted to 200 cc., and  $\text{AgNO}_3$  added to complete precipitation. The precipitate (consisting of the silver salts of the resin and fatty acids) must be protected from sun-light. It is filtered,

\*Benedikt. *Analyse der Fette u. Wachsarten*, p. 121.

†*Amer. Chem. Journ.* **3**, 416.

‡Benedikt. *Analyse der Fette u. Wachsarten*, p. 125.

washed with water, dried at  $100^{\circ}\text{C}$ ., and extracted in a Soxhlet's tube with ether. The silver resinsates dissolve in the ether, while the silver salts of the fatty acids remain behind.

The ethereal solution, as it leaves the extraction tube, should be yellow or light brown in color, but not dark brown. It is filtered, if necessary, and the filtrate shaken with  $\text{HCl}$  in a separatory funnel. The resulting ethereal solution of the resin acids is filtered from  $\text{AgCl}$ , washed with water, and the filter and separator rinsed with ether, the ether distilled off, and the residue dried at  $100^{\circ}\text{C}$ . As the resin is weighed in the hydrated form, its weight must first be multiplied by the factor .9732 to obtain the weight of the anhydride.

The following analyses, lately made according to the methods given, will illustrate their accuracy, as well as the general composition, of the ordinary good laundry soap.

No. 1. A fine white soap, made from lard and tallow.

Water . . . . .	22.19 per cent.
Alkali, combined, as soap ( $\text{Na}_2\text{O}$ ) . . . . .	8.21 "
Alkali, free, as $\text{NaOH}$ . . . . .	.10 "
$\text{Na}_2\text{CO}_3$ . . . . .	.06 "
Total fatty acids as anhydrides . . . . .	69.41 "
	<hr/>
	99.97

No. 2. A white floating soap.

Water . . . . .	16.96 per cent.
Alkali, combined as soap ( $\text{Na}_2\text{O}$ ) . . . . .	9.61 "
Alkali, free, as $\text{NaOH}$ . . . . .	.10 "
$\text{Na}_2\text{CO}_3$ . . . . .	.09 "
Total fatty acids as anhydrides . . . . .	72.92 "
	<hr/>
	99.68 "

No. 3. An ordinary yellow laundry soap, containing resin.

Water . . . . .	19.12 per cent.
Alkali, combined as soap ( $\text{Na}_2\text{O}$ ) . . . . .	8.57 "
Alkali, free as $\text{NaOH}$ . . . . .	.20 "
$\text{Na}_2\text{CO}_3$ . . . . .	.20 "
Residue Insoluble in $\text{H}_2\text{O}$ . . . . .	.20 "
Fatty anhydrides . . . . .	52.32 "
Resin . . . . .	19.45 "
	<hr/>
	100.06 "

No. 4. Similar to No. 3; also containing resin.

Water . . . . .	19.47	per cent.
Alkali, combined as soap ( $\text{Na}_2\text{O}$ ) . . . . .	7.09	"
Alkali, free, as $\text{NaOH}$ . . . . .	2.61	"
$\text{Na}_2\text{CO}_3$ . . . . .	1.76	"
$\text{Na}_2\text{SiO}_3$ . . . . .	.99	"
Fatty anhydrides . . . . .	22.58	"
Resin . . . . .	45.97	"
	<hr/> 100.47	"

No. 4 contained an objectionable amount of free alkali, namely, 2.61 per cent. Probably the sodium silicate used was highly alkaline. The largest amount of caustic alkali in the other soaps examined was .2 per cent.

It is frequently of interest to know the origin of the fatty acids of a soap which is, however, in many cases a problem not easily solved. The only clues are to be sought in the specific gravity, combining weight, melting and solidifying points and iodine number of the fatty acids.

Occasionally, fats, before being used in soap-making, are bleached by various chemical agents, the most common of which are, perhaps,  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ . If now such a mixture is heated in bleaching, as is frequently the case, the  $\text{K}_2\text{Cr}_2\text{O}_7$ , acting on the  $\text{HCl}$  liberates  $\text{Cl}_2$ , and under favorable conditions, the chlorine combines with the unsaturated acids present in the fats as glycerides, thus utterly destroying the value of the iodine number—the most definite index as to the origin of the fats.

Again, it frequently occurs that mixtures of two or more fats may be used, the combining weights, iodine number, and other properties of which closely approximate those of an individual fat, and so an erroneous conclusion may be drawn from an examination of such mixed fatty acids.

If, however, a mixture of two fats, in their natural state, without having undergone any bleaching or refining process, is used, it is generally possible to ascertain, with considerably accuracy, the nature of the fatty acids by means of the iodine number, it having been found by actual experiment that the iodine number of a mixture of two fats corresponds within the limits of analytical error with the theoretical numbers calculated for the pure fats.

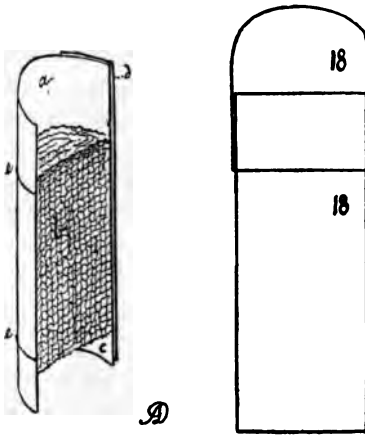
## AN IMPROVED COIL, FOR MILK ANALYSIS.

BY CHARLES RICE, NEW YORK.

The advantage of employing the so-called Adams' coil (of thick blotting paper) in the estimation of milk solids, and particularly of milk fat, is generally recognized; careful trial experiments having shown that, by its use, about 0.2 per cent. more of fat can be extracted from milk than by any other method.

While this fact is undisputed, there remain, however, some slight drawbacks, chiefly mechanical or manipulative, which not seldom inconvenience the operator. These drawbacks arise both from the material the coil is usually made of, and from its shape.

The coils are made of thick blotting paper, the kind generally preferred being that known as "white demy blotting, mill 428, 38 lbs." The best treasury blotting is also used. Now, unless the coil is made rather loosely, which is accomplished sometimes by roll-



Rice's Milk Coil and Weighing Tube.

ing up a thread with the strip of paper, it is not always easy to cause the milk to sink into the coil with sufficient rapidity. Moreover, the shape at either end is not conducive to a rapid absorption, and there is not seldom a loss from milk running down the side or escaping through a central passage.

Several modifications of Adams' coil have been proposed from time to time, one involving the use of asbestos, another that of cotton, but on trial I have found them to offer no material advantages.

A good milk coil, or cartridge, should possess the following properties :

1. It should have a shape which permits the whole amount of the milk taken for analysis (say 5 to 10 gms.) to be applied, or poured upon it quickly, without risk of loss.
2. It should be so porous that it will readily permit the escape

of water, during drying, for the estimation of solids, and afterwards readily admit the ether in the estimation of fat.

The material which I have found to answer best for this purpose is the so-called "absorbent gauze," also known as "bleached hospital gauze," used for surgical dressings. It is a light open-mesh cotton fabric, having about 40 fine threads to the linear inch, and weighing about  $1\frac{3}{4}$  av. ounces per square yard.

The milk coils, or cartridges, which I have been in the habit of using, consist of a small roll of this gauze, enclosed in a wrapper of blotting paper, and their mode preparation is as follows:

Spread out a square yard of the gauze on a flat surface, fold it twice in one direction to reduce it to 36x9 inches then fold it upon the long side in laps of  $1\frac{3}{4}$  inches in width, so that when the whole is folded it will present a strip of one yard in length and about  $1\frac{3}{4}$  to  $1\frac{7}{8}$  inches in width, and will consist of some 18 to 20 layers.

Now begin to roll the strip up on the narrow end, like a bandage, but not too tight, until about 5 or  $5\frac{1}{2}$  inches of the gauze have been rolled up; cut the strip slantingly—that is, not perpendicular to its body, but under an angle, so as not to cause "bunching" when wrapped in paper. Place the roll upon a strip of blotting paper 4 inches long and  $2\frac{3}{4}$  inches wide, and roll the latter over it so as to have it (the paper) project at one end about one-fourth inch over the gauze coil and about three fourths inch at the other: then tie the coil with two threads. It will thus be  $2\frac{3}{4}$  inches long and about seven-eighths inch in diameter.

Fig. 1 represents a section of one of these coils, *b* being the gauze coil, *a* and *c*, respectively, the larger and smaller free compartment, *d* is the overlap of the paper cover, and *e e* the strings.

The larger compartment (*a*) of this cartridge serves as a funnel, into which the full quantity of the milk to be tested is poured at once. A coil of this kind—intended for the smallest size of Soxhlet's extractor—will easily take from 8 to 10 gms. of milk, and the latter will never entirely soak down to the bottom of the paper wrapper. If it should soak to the bottom of the gauze coil, this will do no harm, as it is one-fourth inch above the end of the paper.

These coils may easily be prepared in quantity, then extracted

with ether, and kept in a drying oven, so as to be ready for instant use.

I am in the habit of using very light glass weighing tubes, with snugly fitting covers, each being numbered both on the body and on the cap. A cartridge, perfectly dry, is first weighed in one of these tubes, and all subsequent weighings of it are made in the same tube. The milk to be examined is weighed in a separate stoppered graduated tube, then a suitable quantity of it, judged by guess and experience—corresponding to, say, about 8 gms.—is poured into the compartment *a* of the coil, which had previously been taken from the weighing tube. The graduated tube is weighed again, and the difference corresponds to the milk taken for analysis. The coil at once absorbs the milk, and is then transferred on a capsule to the drying oven. When dry it is weighed for determination of solids, and the fat then determined by extraction with ether in the usual manner.

The size of these cartridges may of course be varied according to the size of the extractor in which they are to be used.

I am quite certain that those who will try the gauze coils will prefer them to anything else heretofore proposed.

NEW YORK, FEBRUARY 12, 1890.

#### NOTE ON STILBITE FROM YORK HAVEN, YORK COUNTY, PA.

BY C. H. EHRENFELD.

This mineral has not been reported heretofore from the above mentioned locality. It occurs in granite, in veins varying from about a thirty-second to a quarter of an inch in thickness. It is white, translucent to transparent, with pearly lustre and radiated crystalline structure.

The average of two sp. gr. determinations is 1.825. Analysis showed the following composition :

H <sub>2</sub> O	15.25%
SiO <sub>2</sub>	47.20
Al <sub>2</sub> O <sub>3</sub>	19.01
CaO	16.72
K <sub>2</sub> O	2.39
Na <sub>2</sub> O	0.00

Total . . . . . 100.57

It will be noticed that the percentage of CaO is unusually high, and that of SiO<sub>2</sub> correspondingly low.

## XI. A NEW METHOD FOR THE ESTIMATION OF THEINE IN TEAS.

BY G. L. SPENCER.

The majority of methods for the estimation of theine are either extremely tedious or the theine obtained is contaminated with coloring matter and other impurities. Many of the methods require extraction in a percolator from 24 to 48 hours. This, together with the numerous transfers from one vessel to another, are decided objections. In the work for the U. S. Department of Agriculture, after losing considerable time in experimenting with various methods, I adopted the following:

Take 2 to 3 gms. of finely powdered tea in a small beaker, cover this with water to a depth of 3 or 4 centimeters, and boil; set aside for the particles of tea to settle, then decant the solution; repeat this extraction seven times. Transfer the residue to a filter and wash with a few cubic centimeters of boiling water, and add the filtrate to the solution already obtained.

It is important that a considerable quantity of water be used in the first extraction, smaller quantities being used afterwards. To the solution obtained, add subacetate of lead. About .8 cc of the concentrated lead solution is usually required. Filter off the precipitate and wash it with hot water; remove the lead by  $H_2S$ ; concentrate the filtrate to approximately 50 cc., having first added about .5 gms. of magnesia or hydrate of calcium. Filter, washing the residue with hot water, and collect the filtrate in a separatory funnel. After the solution has cooled sufficiently, extract seven times with chloroform. Collect the chloroform solution of the theine in a small tared flask and remove the solvent by distillation. Dry the theine at  $75^\circ C.$  and weigh. The theine obtained by this method is very pure.

In the *Zeit. f. anal. Chemie*, **28**, 257, Hilger describes a similar method for the estimation of theine, which differs though in certain essential conditions. The method above described was in use in the Department of Agriculture before that of Hilger was received.

Mr. T. F. Sanborn of this Department has obtained excellent results by this new method on a large number of teas. His results agree closely with parallel work by some of the longer but equally accurate methods.

## SOME POINTS IN THE DETERMINATION OF SILICA IN SILICATES BY FUSION WITH ALKALINE CARBONATES.\*

BY JAMES P. GILBERT, S. B.

The usual method of determining silica in silicates—that of fusion with the alkaline carbonates, decomposition with hydrochloric acid, and subsequent evaporation to dryness—does not always give satisfactory results. This method is universally described in the text-books as being accurate, with the occasional caution that the filtrate should also be examined for any silica which may not have been rendered insoluble by evaporation to dryness. But one looks in vain for any intimation of what may be the amount of the error, in the determination of silica as usually carried out, if one neglects to examine the filtrate. There is no doubt that many chemists have had trouble with this method, and some have given it up, preferring to volatilize the silica with hydrofluoric and sulphuric acids, and, after a careful analysis of the residue, to calculate the silica by difference. A recent writer† makes the statement that he has never been able to obtain more than 97.5 per cent. of the total silica in highly siliceous bodies by the fusion method. The following work was undertaken in the hope of discovering some of the sources of error in the fusion process.

The influence of the temperature at which the silica is dehydrated was first investigated. Most authorities say that evaporation on the water bath to complete dryness, or until no more hydrochloric acid is given off, is sufficient to dehydrate the silica, but a few recommend subsequent heating in an air-chamber to a temperature of 110° C. A higher temperature than 110° C. is said by Fresenius to be inadmissible, since there is liability of the silica recombining with the bases present to form silicates partially decomposable with hydrochloric acid.

To test the influence of temperature on the amount of silica obtained, the following determinations of silica were made in a blast-furnace slag containing about 46 per cent. of lime, 10 per cent. of alumina, and less than one per cent. of magnesia. The silica was dehydrated at various temperatures, but in all other respects the process was carried out exactly as Fresenius directs. What is

\*Technology Quarterly, February, 1890.

†George Craig: Chem. News, Vol. LX, No. 1563.



generally called silica, that is, the mass insoluble in hot hydrochloric acid after evaporation to dryness, is given in Column I. of the following table. This was treated with hydrofluoric acid and the weight of the residue is given in Column II. In the filtrate from the silica the alumina was precipitated by ammonia, dried, ignited, and then fused with potassium bisulphate. The residue left on treating the fused mass with water, (and correcting for the impurities of the bisulphate used,) is given in Column III. The total silica in Column IV. is calculated by subtracting the weight of the residue left after treatment with hydrofluoric acid from the weight of the silica as given in I., and adding that found with the alumina in Column III.

*Table No. I.—Analyses of Blast-furnace Slag (containing 46 per cent. Lime) by Fusion with Alkaline Carbonates.*

	I. Residue insoluble in hydrochloric acid after evaporation to dryness.	II. Weight of residue obtained from treating Column I. with hydrofluoric acid.	III. Weight of Silica found in Alumina.	IV. Total Silica.		I. Residue insoluble in hydrochloric acid after evaporation to dryness.	II. Weight of residue obtained from treating Column I. with hydrofluoric acid.	III. Weight of Silica found in Alumina.	IV. Total Silica.
	Per cent.	Grams.	Grams.	Per cent.		Per cent.	Grams.	Grams.	Per cent.
1	41.25	.0003	.0006	41.26	9	41.33	.0013	.0005	41.25
2	41.34	.0024	.0008	41.17	10	41.71	.0036	.0007	41.42
3	41.39	.0012	.0009	41.33	11	41.53	.0028	.0007	41.27
4	41.32	.0020	.0003	41.18	12	41.89	.0031	.0004	41.35
5	41.22	.0012	.0009	41.19	13	41.79	.0032	.0002	41.41
6	41.43	.0021	.0007	41.23	14	41.65	.0027	.0005	41.43
7	41.40	.0014	.0009	41.32	15	41.90	.0028	.0001	41.48
8	41.48	.0017	.0008	41.35					

Nos. 1 to 3 inclusive were dehydrated on the water bath.

Nos. 4 to 6 inclusive were dehydrated at 125° C.

Nos. 7 to 9 inclusive were dehydrated on iron plate over Bunsen burner.

Nos. 10 to 15 inclusive were dehydrated in air-chamber at 280° C.

All evaporations were made in porcelain.

In this series of results it will be seen that the silica was practically all rendered insoluble even at the temperature of the water bath, and that there was no gain in this respect in using a higher temperature. But the amount of foreign matter in the silica was, in general, perceptibly higher at the higher temperature of dehydration. This is probably due to the alumina being rendered partially insoluble in acid. From the fact that very little silica was found in the alumina, it would seem as if there were no tendency for the silica to recombine with the lime and alumina even at a temperature of 280° C. Nos. 13, 14, and 15 were digested, after dehydration, with hot acid for one hour, in the expectation of dissolving out all the alumina and other bases, but this treatment did not give smaller residues, after the volatilization of the silica with hydrofluoric acid, than in Nos. 10, 11, and 12, which were treated only thirty minutes with acid.

Table II.—Analyses of a Blast-furnace Slag (containing 35 per cent. Lime and 15 per cent. Magnesia.

	I. Residue insoluble in hydrochloric acid after evaporation to dryness.	II. Weight of residue obtained from treating Column I, with hydrofluoric acid.	III. Weight of Silica found in Alumina.	IV. Total Silica.		I. Residue insoluble in hydrochloric acid after evaporation to dryness.	II. Weight of residue obtained from treating Column I, with hydrofluoric acid.	III. Weight of Silica found in Alumina.	IV. Total Silica.
	Per cent.	Grams.	Grams.	Per cent.		Per cent.	Grams.	Grams.	Per cent.
1	33.65	.0032	.0032	33.61	7	33.49	.0032	.0011	33.24
2	32.90	.0014	.0025	33.18	8	33.85	.0045	.0012	33.27
3	33.46	.0013	.0013	33.29	9	33.90	.0042	.0012	33.30
4	33.71	.0027	.0004	33.40	10	33.65	.0062	.0062	33.62
5	33.42	.0021	.0008	33.24	11	33.83	.0046	.0045	33.80
6	33.75	.0031	.0004	33.36	12	33.95	.0088	.0050	33.60

Nos. 1 to 3 inclusive were dehydrated on the water bath.

Nos. 4 to 6 were dehydrated at 120° C.

Nos. 7 to 9 inclusive were dehydrated on iron plate, over Bunsen burner.

Nos. 10 to 12 inclusive were dehydrated at 280° C.

The general uniformity of the results in this series suggested the possible influence of the calcium chloride present in dehydrating the silica on evaporation to dryness. This led to the second point considered, namely, the influence of the salts present on the determination of silica. It is not unreasonable to suppose that some salts, such as calcium chloride, may have a beneficial influence, while others, as, for example, magnesium chloride, which is decomposed when its solution is evaporated, may vitiate the silica determination by forming a silicate which will be subsequently decomposed by hydrochloric acid with solution of the silica. To test the effect of magnesium chloride, determinations of silica were made in a slag containing about 35 per cent. of lime, 15 per cent. of magnesia, and 15 per cent. of alumina. (See Table II.)

This series differs from the first mainly in the large amount of impurity in the silica and the large amount of silica in the alumina when the dehydration is effected at a temperature of 280° C. The best results were obtained at a temperature of 120° C. The increase of silica in the alumina as the temperature is increased

*Table III.—Analysis of a Sample of Orthoclase.*

	I.					II.			
	Residue insoluble in hydrochloric acid after evaporation to dryness.	Weight of residue obtained from treating Column I. with hydrofluoric acid.	Weight of Silica found in Alumina.	Total Silica.		Residue insoluble in hydrochloric acid after evaporation to dryness.	Weight of residue obtained from treating Column I. with hydrofluoric acid.	Weight of Silica found in Alumina.	Total Silica.
	Per cent.	Grams.	Grams.	Per cent.		Per cent.	Grams.	Grams.	Per cent.
1	64.80	.0018	.0004	64.52	5	64.98	.0050	.0019	64.45
2	64.13	.0018	.0030	64.30	6	64.62	.0035	.0020	64.36
3	64.03	.0026	.0035	64.20	7	64.83	.0068	.0030	64.45
4	64.35	.0020	.0030	64.52	8	64.97	.0083	.0039	64.35

Nos. 1 and 2 were dehydrated on the water bath.

Nos. 3 and 4 were dehydrated at 120° C.

Nos. 5 and 6 were dehydrated on iron plate over Bunsen burner.

Nos. 7 and 8 were dehydrated at 280° C.

would seem to be due to the magnesia, for the conditions were, in all other respects, the same as in the analyses of the other slag. The above results indicate that there is no danger of the silica combining with the magnesia at  $120^{\circ}$  C., and that at this temperature the silica is almost completely dehydrated, the calcium chloride probably assisting in the dehydration.

A series of analyses was next made on orthoclase, practically free from lime and magnesia.

This series differs from the previous one in that the higher temperature is not accompanied with an increased amount of silica in the filtrate. This would seem to be a confirmation of the idea that there was a recombination of the silica and the magnesia at the temperature of  $280^{\circ}$  C. in the magnesia slag; and the fact that the amounts of silica found in the alumina are (with one exception) uniformly higher than those in the lime slag indicates, I think, the beneficial effect of the calcium chloride in the dehydration of the silica.

The third point considered was the influence of temperature on the dehydration of the silica when no bases other than the alkalies were present. From the last three series of analyses it would seem that some silica always fails to be rendered insoluble by heat alone, so that, if a definite amount of pure silica were taken and subjected to alternate fusions and dehydrations, we should expect that the amount of silica obtained would diminish at each successive treatment. To ascertain if this were so, two determinations of silica were made in the lime slag, and the silica thus obtained repeatedly treated by fusion with alkaline carbonates in the usual way. The per cent. of silica recovered in each case is given below. The silica obtained from the slag by the first fusion and dehydration is taken as 100 per cent.

	I. Per cent.	II. Per cent.	
1.	42.02	41.81	{ Silica in slag obtained by heating to $280^{\circ}$ C.
2.	97.24	97.79	
3.	96.04	96.70	{ Percentage of the above obtained in four successive fusions by heating to $120^{\circ}$ C.
4.	95.17	95.96	
5.	94.19	95.45	

The large difference between the results of the first and second fusions is probably due to impurities in the silica, which was

heated to  $280^{\circ}\text{C}$ .; but the variations in the other cases can only be due to loss of silica by incomplete dehydration. Still, these are better results than Craig obtained, who does not, however, mention the temperature he used in dehydrating the silica.

The fourth point considered was the possibility of obtaining the silica in a pure state, that is to say, to decrease the amount of the residue left after treatment with hydrofluoric acid. This residue may be due to imperfect washing, or to the fact that alumina has been rendered insoluble in hydrochloric acid by prolonged heating to a high temperature. The higher residues obtained in the cases in which the silica was heated to  $280^{\circ}\text{C}$ . point to the latter possibility. But it is not improbable, as will be mentioned later on, that under certain conditions the silica may enclose alkaline salts so that it is impossible to remove them completely by washing.\*

In an interesting article by Lindo,† on the analysis of glass, I met the recommendation that the watery solution of the fusion be diluted to a very large bulk, so that on acidifying with hydrochloric acid there shall be no precipitation of silica. In this way he obtained, on evaporation, what he called "vitreous silica," in distinction from the ordinary "amorphous silica." This vitreous silica, he says, is so easily washed that time is gained in the analysis to compensate for that lost in the evaporation of the solution. Lindo takes it for granted that one cannot get all the silica by the ordinary process of dehydration, and that the last traces of it cannot be got out of the filtrate unless there is sufficient iron oxide or alumina present to effect its complete precipitation. In the analysis of glass, he added a known amount of ferric chloride to the filtrate from the alumina, and by precipitating this iron with ammonia the last traces were obtained.

The following analyses of glass were made according to his directions. The powdered glass, about one gram, was fused with five grams of sodium and potassium carbonates, and the mass treated with about four hundred cubic centimeters of boiling water until it was thoroughly disintegrated. On acidifying with hydrochloric acid, a clear solution was obtained. This was evap-

\*In this connection it is interesting to note that all the residues left on treatment with hydrofluoric acid, in the two slags analyzed, contained manganese, which may point to an insoluble compound of manganese with the alkaline salts.

†Chemical News, Vol. LX. No. 1546.

orated to dryness on a water bath, heated to  $125^{\circ}$  C., and, as recommended by Lindo, the silica thus obtained again fused and treated as before. This silica obtained from the second fusion was weighed, and then treated with hydrofluoric acid. The two filtrates were combined and evaporated to dryness, heated to  $125^{\circ}$  C. for one hour, and the residue, insoluble in hydrochloric acid and water, filtered off; this is given in the third column. The first three analyses are of German "half-white" glass; the last two, of Bohemian white glass.

*Table IV.—Determinations of Silica in Glass. (Lindo's Method.)*

	I. Silica obtained after two fusions.	II. Residue from Column I. with hy- drofluoric acid.	III. Silica obtained from the filtrates.	IV. Total Silica.
	Per cent.	Grams.	Grams.	Per cent.
1	73.03	.0003	.0058	73.58
2	71.81	.0008	.0125	73.06
3	72.50	.0004	.0084	73.22
4	71.96	.0000	.0051	71.43
5	71.25	.0007	.0060	71.70

In this case it is seen that a considerable portion of the silica fails to be dehydrated by one evaporation and heating to  $125^{\circ}$  C. The silica obtained in this way is very compact, and the washing, as claimed by Lindo, is very easily done. The purity of the silica thus obtained (shown by the small residue left on treatment with hydrofluoric acid) is doubtless in part due to the facility with which the silica is washed; for it is conceivable that, when the silica is separated from a concentrated solution of alkaline salts, it may enclose particles of the liquid which may not be easily washed out. But this high purity, as compared with the silica obtained from the slags and the feldspar, may be due to the absence of any large amount of alumina in the glass.

To see what would be the character of the silica obtained from the first slag by large dilution of the solution of the fused mass before acidifying, the following determinations were made.

## DETERMINATION OF SILICA.

Table V.—Amount of Foreign Matter in Silica obtained from Lime Slag. (*Lindo's Method.*)

I.		II.	
Weight of Silica obtained from Slag.		Residue from Column I, with hydrofluoric acid.	
Grams.		Grams.	
1.	.2755	.0008	} Silica obtained by evaporation to dryness on water bath.
2.	.2610	.0010	
3.	.2871	.0008	} Silica obtained by evaporation to dryness and heating to 125° C.
4.	.2683	.0012	
5.	.2506	.0036	} Silica obtained by evaporation to dryness and heating to 280° C.
6.	.3113	.0043	

These figures would seem to justify the inference that in the presence of considerable alumina it is not possible, even by large dilution, to get as pure silica as is easily obtained when only salts of the alkalies or alkaline earths are present.

The foregoing determinations confirm the statement that the ordinary process of fusion with alkaline carbonates and evaporation to dryness cannot always be relied on to render all the silica insoluble. No experiments were made to determine the effect of *repeated* evaporations to dryness with hydrochloric acid.

When the evaporation is carried out in the presence of free sulphuric acid the results are more satisfactory, but, as Craig says, the amount of alkaline sulphates introduced seriously interferes with the determination of the bases present.

A comparison of results obtained from a sample of quartz by evaporation with hydrochloric and sulphuric acids is given below.

I.		II.	
Silica by evaporation to dryness with hydrochloric acid and heating to 120°.		Silica by evaporation to dryness with sulphuric acid.	
Per cent.		Per cent.	
98.95		99.43	
98.60		99.67	
98.79		99.51	
		99.70	

In these determinations I followed Lindo's recommendation of diluting largely before acidifying, and the residue left, on treatment with hydrofluoric acid, was very small. The first two determinations by sulphuric acid were done by decomposing the dilute watery solution of the fusion with hydrochloric acid, evaporating to dryness, and then adding strong sulphuric acid in ex-

cess and heating on an iron plate until copious fumes of sulphuric acid were given off for several minutes. The silica was in appearance the same as obtained by Lindo's method with the aid of hydrochloric acid only. But in the last two the watery solution of the fusion was decomposed directly by sulphuric acid in considerable excess, and then evaporated as before. The silica obtained in this way was bulky and gelatinous.

These results seem to justify the recommendation that has been made; namely, that in the analysis of silicates the silica is best determined by dehydration with sulphuric acid (in cases where it is not inadmissible by the presence of lime, barium, lead, etc.), and that the bases should be determined, after the decomposition of the silicate, by hydrofluoric acid.

MASS. INSTITUTE OF TECHNOLOGY,  
January, 1890.

## RAPID DETERMINATION OF BROMINE IN PRESENCE OF CHLORINE.

BY CHARLES C. HALL, MIDDLEPORT, OHIO.

The writer had occasion a few months ago to determine the amount of bromine in the bittern from some salt works. Time and facilities being limited, a procedure was adopted that gave satisfactory results at the time, and has since been tested on solutions containing known amounts of bromine.

The method involves no new principle, but differs in the application of a familiar reaction from any method at present published—at least so far as I know. But I must confess to limited literature on the subject.

The procedure is to liberate the bromine with chlorine water and absorb it in chloroform; continue the addition of chlorine water until the chloroform takes the pale yellow color produced by the bromine chloride that is eventually formed.

The chlorine water is prepared by saturating cold distilled water with washed chlorine, and should be kept in the dark, but should not be depended on after any great length of time.

Dissolve some fused potassium bromide in water in the proportion of 14.8750 gms. per liter. 1 cc. of this solution contains .01 gm. bromine, and is used to standardize the chlorine water, as follows:



Take a glass stoppered tube of about 50 cc. capacity graduated from the bottom and introduce from a burette 3 or 4 cc. of the potassium bromide solution, and 2 or 3 cc. of water ; add the chloroform in proportion of 1 cc. for every .03 gms. of bromine present. Run in the chlorine water from a burette about 3 cc. at a time while the bromine is being liberated, and after each addition of the chlorine insert the stopper in the tube and shake violently. While there is unliberated bromine present, each addition of chlorine water will cause a red color to appear. After complete liberation of the bromine the chlorine water renders the liquid colorless. The point is easily noticed, and will guide the operator in the addition of the chlorine water, as twice as much chlorine water is necessary to complete the reaction as is necessary to liberate the bromine. A color standard can be made by dissolving 1 gm. bichromate of potassa in 20 cc. pure water. The color thus produced can be matched in the chloroform. A lighter color can be used, but this seems preferable, as an excess of chlorine is recognized by giving the chloroform a lighter color than the standard.

The sample to be tested is treated in a similar manner. Care should be taken to keep the amount of bromine near the amount used in standardizing. One or two trials will show what bulk of the sample to take.

The colors should be observed by holding the tube against a white background, similar to other determinations by color. It will aid accuracy to have the burette delivering the chlorine water painted black, and to test the strength of each burette full. A 50 cc. burette holds enough to be standardized, and titrate in duplicate an ordinary analysis. .04 gms. bromine require about 15 to 16 cc. chlorine water.

The only skill required is to recognize the end of the reaction as indicated by the color of the chloroform, but this is not more difficult than the colorimetric method for carbon in steel.

Chloroform is preferable to ether, as it sinks to the bottom of the tube and does not evaporate to any extent. It can be recovered by collecting, shaking with a little potassium hydrate solution to remove bromine, washing and distilling.

Appended are a few *consecutive* results obtained by working on solutions of potassium bromide and salt. These solutions were

prepared by an assistant and the amount of bromine unknown until after the results were obtained.

Most of the results are close. Those with the greater variance would have been discovered if duplicates had been made.

No.	Amount of Bromine in the Solution.	Amount of Bromine Found.
1 . . . . .	.060 gms.	.058 gms.
2 . . . . .	.023 "	.023 "
3 . . . . .	.050 "	.054 "
4 . . . . .	.034 "	.037 "
5 . . . . .	.013 "	.013 "
6 . . . . .	.031 "	.029 "
7 . . . . .	.013 "	.013 "
8 . . . . .	.034 "	.031 "
9 . . . . .	.031 "	.030 "
10 . . . . .	.014 "	.013 "
11 . . . . .	.035 "	.036 "
12 . . . . .	.016 "	.016 "
13 . . . . .	.033 "	.034 "
14 . . . . .	.046 "	.044 "
15 . . . . .	.021 "	.021 "
16 . . . . .	.032 "	.032 "
17 . . . . .	.033 "	.032 "
18 . . . . .	.060 "	.059 "
19 . . . . .	.045 "	.044 "

## LABORATORY APPARATUS.\*

### HYDROGEN GENERATOR.

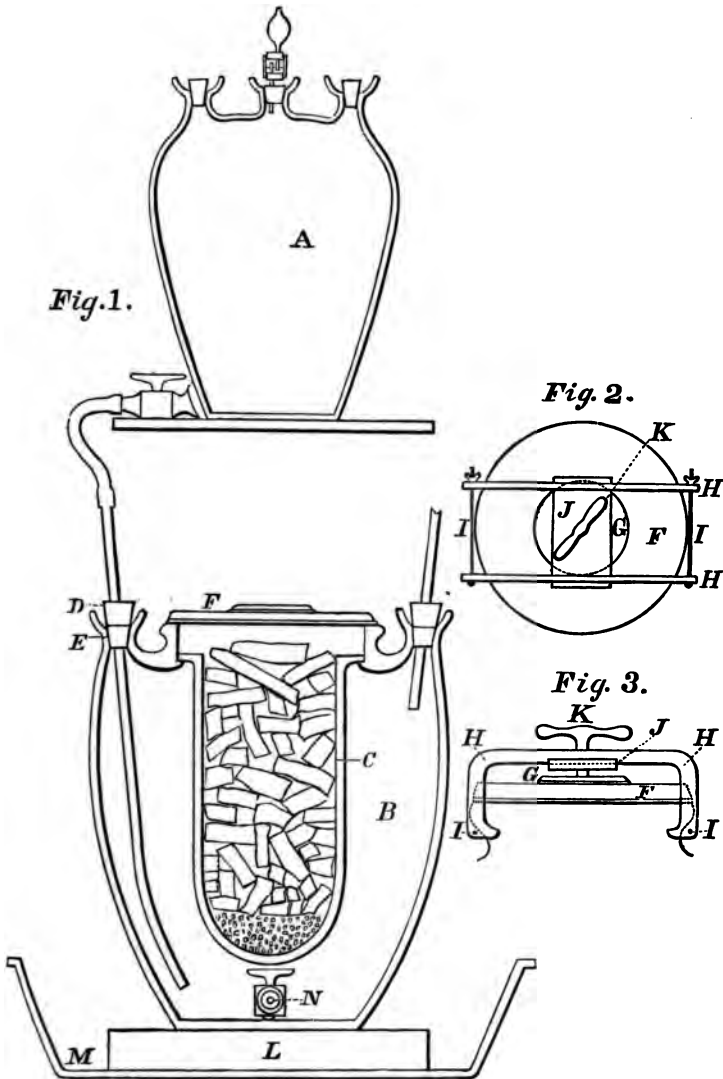
By S. W. JOHNSON AND T. B. OSBORNE.

A full supply of some inert gas is necessary in agricultural chemical laboratories for making moisture determinations with accuracy. Hydrogen by reason of its rapidity of diffusion and the ease of obtaining it in a state of comparative purity has decided advantages over any other gas. The ordinary Kipp generator and other portable apparatus do not supply enough gas nor sufficient pressure for this use.

The accompanying figures 1, 2 and 3 represent an apparatus which has been in use for about three years with most satisfactory results. The principle of its construction is the same as of the Kipp generator. The three vessels *A*, *B* and *C*, Fig. 1, are of

\*From the Annual Report of the Connecticut Agricultural Experiment Station for 1889.  
Revised by S. W. Johnson, Director.

stone ware and were bought of Messrs. Eimer & Amend of New York. *A* is No. 8456 of their catalogue, "Woulff's Bottle of best German acid-proof stone-ware," capacity 8 gallons. *B* is No. 5954*a*, "Chlorine apparatus of acid-proof stone ware, with ground air tight cover," capacity 20 gallons, and the perforated inside vessel, *C* is No. 5954*b*. *B* should be ordered with "outlet near the bottom and ground-in stop cock. The stone ware basket *C* within *B* is perforated with many  $\frac{1}{2}$  inch holes. In the bottom of *C* is placed a layer of coarse quartz gravel four or five inches deep. On this are laid 100 pounds of zinc spelter—broken ingots—as shown in the figure. The acid-reservoir *A* stands on a bracket shelf covered with sheet lead, directly above *B* so that any leakage may fall into the sink *M* below. The three necks of *A* are closed with rubber stoppers, the central one provided with a glycerine valve, seen in the figure, which admits air and hinders the escape of acid fumes. The pressure of gas is regulated by the height of the reservoir *A*. In our arrangement, a distance of only  $3\frac{1}{4}$  feet between the bottoms of *A* and *B* was available, and this has proved sufficient. *A* is connected with *B* by a stout glass tube one inch in diameter, which goes nearly to the bottom of *B*. It is joined to the stop cock of *A* by a tight fitting piece of rubber hose which has been thoroughly soaked in a mixture of melted paraffine and vaseline. To enter *B* this tube passes loosely through a wooden collar, *D*, about 3 inches long and tightly through a rubber stopper, *E*, which is driven well down into the tubulure. The collar and stopper are securely tied down by stout copper wire to the neck of the tubulure. This fastening is not shown in the figure. The cup-shaped cavity above the stopper is finally filled with a melted mixture of paraffine and vaseline (having when cold the consistency of soft lard) so as to completely cover the rubber. The leaden exit tube of  $\frac{1}{2}$  inch bore for the hydrogen gas shown on the opposite side of *B* is similarly secured. It is carried some 20 feet to a table in the laboratory on the floor above, where it is provided with a very carefully ground brass stop cock. In this way perfectly gas-tight joints capable of resisting the pressure of the apparatus are obtained without difficulty. The cover of *B*, see sectional drawings, Figs. 2 and 3, is made of cast iron  $\frac{3}{4}$  inch thick in order to sustain the strain of



the heavy clamps required to hold it in place. The earthen ware cover furnished with the jar was found to be too weak. Beneath the cover *F* which is planed to a true surface is a thick sheet of soft vulcanized rubber thoroughly impregnated with the melted

paraffine-vaseline mixture. Above *F* is an iron disc *G* about six inches in diameter, separated from *F* by a rubber disc to equalize pressure. Two steel clamps *HH* tied together by iron screw-bolts, *II* to keep them in position, rest on a wrought iron plate  $\frac{1}{2}$  inch thick *J* whose ends are turned up as indicated in Fig 3. Through the center of *J* passes the screw *K*  $\frac{1}{2}$  inch thick with a transverse handle. The end of the screw bears upon the disc *G*. The ends of the clamps embrace the stout flange about the mouth of the stone-ware vessel and are well fitted to its contour.

The sheet rubber beneath the cover *F* serves not only to pack the joint but also to protect the iron from corrosion by the acid in the vessel beneath. The vessel *B* rests on a large fire brick *L* soaked in melted paraffine and this in turn stands in a heavy iron sink *M* well painted with asphalt. This iron sink (for which one of acid-proof stone-ware might be advantageously substituted), is bedded in mortar on a low brick platform on the cellar floor and its outlet is trapped into the drain.

The use of hydrochloric acid so diluted with water that it scarcely fumes (specific gravity 1.11) avoids the crystallization of zinc-salts in the apparatus. To charge this generator the stop-cock of *A* is opened and acid is poured in till the vessel is three-fourths filled. When by use the acid is exhausted, the cock *N* is opened, the zinc chloride solution discharged into the sink and fresh acid is supplied through one of the tubulures in *A*.

Since setting up the apparatus about three years ago, the supply of hydrochloric acid has been several times renewed, but the vessel *B* has not been opened and the charge of zinc is apparently far from being exhausted. It was to avoid the annoyance of frequent replenishment and repairs that this apparatus was constructed, and the care exercised to make it gas-tight and durable has been well bestowed.

#### GAS DESICCATOR.

By S. W. JOHNSON.

This apparatus was designed primarily for drying hydrogen to be used in determining water in vegetable products. It has proved very convenient and time-saving in the lecture room, as well as in the laboratory for exposing gases to liquid absorbents. It consists of nine parts, wholly of glass, viz., the waste-acid jar

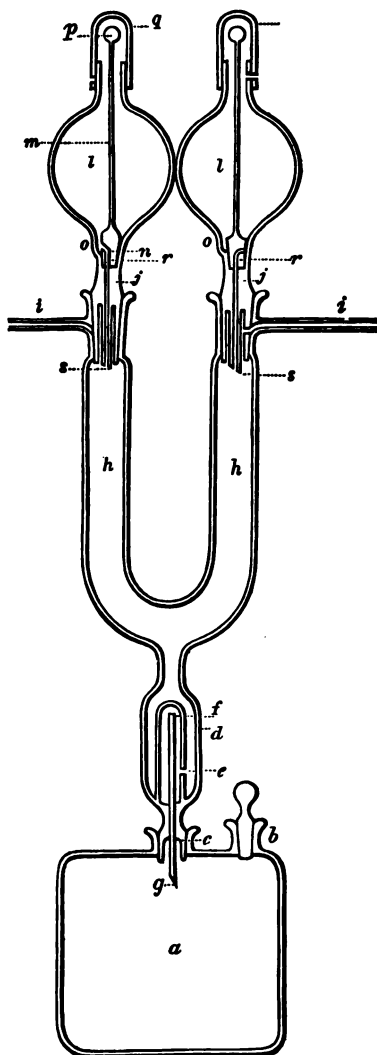


Fig. 4.

*a*, fig. 4, and ground glass stopper *b*, the U-tube *h* with its accessory parts, the acid bulbs *l*, the cocks *m* and the caps *q*. The apparatus was made in Germany to order by Messrs. Eimer & Amend, and cost, duty free, between \$6 and \$7 when several were

ordered at once. *a* is a cylindrical jar  $5\frac{1}{4}$  inches in diameter and  $5\frac{1}{2}$  inches high, having a tubulure with ground glass stopper *b* for emptying the waste acid. The U-tube is fitted to *a* by a hollow ground glass stopper. Immediately above this is a trap whose construction is sufficiently plain from the figures. Instead of the solid stopper at *b*, a cap similar to *qq* should be provided. When acid trickles into this trap it rises in the outer bulb *d* and passing through *e* rises equally in the inner bulb till the level is above the top of the tube *fg* through which it discharges in *a*. The U-tube *hh* is 8 inches high from *f* to *s* and 1 inch in diameter, *i* and *i* are ingress and egress tubes. Each acid bulb *l* is fitted to the U-tube by the hollow ground-glass stopper *j*. In each stopper is a single perforation which by turning the bulb may be brought to coincide with the tubes *i* and *i* and so admit gas to the U-tube. This is shown on the right of the figure. The gas is shut off by turning each bulb slightly. Through *l* passes a glass rod *m* enlarged and flattened at *p* for convenience in turning. The lower part of this rod is enlarged and carefully ground to make a tight stopper at and above *r* except at one point *o* where the wall of the acid bulb is expanded a little. In this section of the stopper is a perforation *n*. The perforation continues through the bulb-neck *j* to *s*. It is evident that if *l* contains acid and *p* is turned till the hole *n* is opposite *o*, passage will be opened between *l* and *h*. *qq* are caps ground to fit the shoulder of the bulbs with perforations as indicated to exclude or admit the atmospheric air. For use the apparatus is supported on a stout iron lamp-stand to whose upright each arm of the U-tube is held by a clamp. All the joints except those at *o* are smeared lightly with vaseline. The U-tubes are filled with beads or sections of glass tube about  $\frac{1}{4}$  of an inch long,  $\frac{1}{4}$  inch in diameter, with bore of about  $\frac{1}{8}$  inch. All the cocks being closed, the bulb tubes are filled with the strongest commercial oil of vitriol,\* *b* is next opened and then by turning *p* and *p* acid is allowed to run over the beads in the U-tube and fill the trap *d* till it begins to discharge into *a*. The cocks are again closed as also *qq* and *b* and the apparatus may then be set aside till needed, and will keep in condition for immediate use for an indefinite time.

\*We now use an acid of 97 per cent.  $H_2SO_4$  obtained from the Fairfield Chemical Co., 71 Wall St., N. Y., for two cents a pound by the carboy.

When needed for use the hydrogen supply tube is joined with one of the tubes *i*, and the other tube *i* is connected as required, *b* is loosened and by turning *p* and *p*, acid is made to drop slowly over the beads in *h* and out from the trap into *a*. Next, both the acid bulbs are turned to open passage through the U-tube and the hydrogen is turned on at a suitable rate of flow. As the gas enters it is exposed to a large surface of concentrated oil of vitriol which does not grow sensibly weaker as in other forms of apparatus, because always renewed. As the gas leaves the U-tube it encounters a similar current of fresh oil of vitriol.

The following data show the efficiency of this apparatus in drying hydrogen: A stream of hydrogen was passed through a wash-bottle containing 40 per cent. sodium hydrate solution, to retain a possible trace of hydrochloric acid or hydrogen sulphide and also to indicate the rate of flow, then through this drying apparatus, and afterwards through a weighed U-tube filled with broken glass, drenched with pure sulphuric acid which had been boiled in platinum to concentrate and contained 94.17 per cent. of  $\text{H}_2\text{SO}_4$ . This was slightly stronger than the acid used in the drying apparatus at the time. Hydrogen was passed through the apparatus at a measured rate while each of the bulbs of the drying tubes delivered a certain number of drops of oil of vitriol per minute. The results of several experiments, in which the weight of the U-tube remained fairly constant within the ordinary limits of error, are given in the following table.

No. of experiments.	Rate of flow of hydrogen No. of minutes per liter.	No. of liters of hydrogen passed.	Flow of oil of vitriol in apparatus. No. of drops per minute.	Time of experiment in minutes.	Gain or loss of weight of U-tube in grams.
1	4½	14.4	18-20	60	+ .0003
2	4½	13.3	11-12	60	— .0005
3	3½	8.5	6- 7	30	— .0009
4	3½	8.5	6- 7	30	— .0001
5	2½	24.0	5- 8	60	.0000

#### APPARATUS FOR DRYING IN HYDROGEN.

BY A. L. WINTON.

This apparatus has been in use for a year and a half. *A* in fig. 5 is a rectangular copper boiler 9 inches long, 9 inches wide and 7 inches deep, supported by iron legs. *B* is a stopcock, through which the boiler can be emptied, and which carries a glass gauge



attached by a rubber stopper, for showing the water level. Through the short tube *C* a thermometer may be introduced. *D* is a copper tube connecting with a block tin coil inside the condenser tank *E*, which is 9 inches long, 5 inches wide and 4 inches deep, and is held 3 inches above the boiler by copper supports. When in use, cold water is supplied to this condenser to prevent loss by evaporation from the boiler. Eight copper tubes *G*, arranged as in the figure, pass through the boiler horizontally. They are  $\frac{9}{16}$  inch inside diameter and as long as the width of the boiler, 9 inches, and their open ends are soldered flush with the sides of the latter. The copper brackets *F* support the metal tubes *I*, through which hydrogen is supplied.

Fig. 6 shows four of the eight glass drying tubes *G*, attached by rubber connectors *H* to the copper tube *I*, and ready for insertion into the tubes *G* of fig. 5. These glass tubes, each numbered and provided with numbered cork stoppers, are eight inches long and about  $\frac{1}{2}$  inch in outside diameter. For use, a small cotton plug closes the throat of the tube at *J*. The finely pulverized air-dry material (two grams) in which a water determination is to be made, is weighed on a watch glass and poured in through a funnel, or introduced directly from a weighing tube, another small cotton plug is inserted and the cork stoppers are put in place. The tubes are wiped and after 20 minutes, are weighed. They are then fitted with perforated stoppers *K*, carrying glass tubes which are drawn out to fine jets and are connected by rubber with copper tubes *I*. These tubes of  $\frac{1}{4}$  inch bore are closed at one end and have branch offsets of the same diameter as the glass tubes. A three-way glass tube with rubber connectors joins two of these copper tubes to each other and to the hydrogen supply. At first the tubes are so placed that the glass jets do not project beyond the side of the boiler; otherwise the moisture will condense in them. A slow current of dry hydrogen displaces the air, and after most of the moisture is gone, the jets are made to project and the gas is lighted to show that it traverses all the tubes. If the pressure is sufficient there will be no difficulty in distributing the hydrogen. The boiler, filled to *G*, with water, to which sodium nitrate may be added if necessary to raise the boiling point to 100° C. or higher as desired, is heated by a gasburner. The

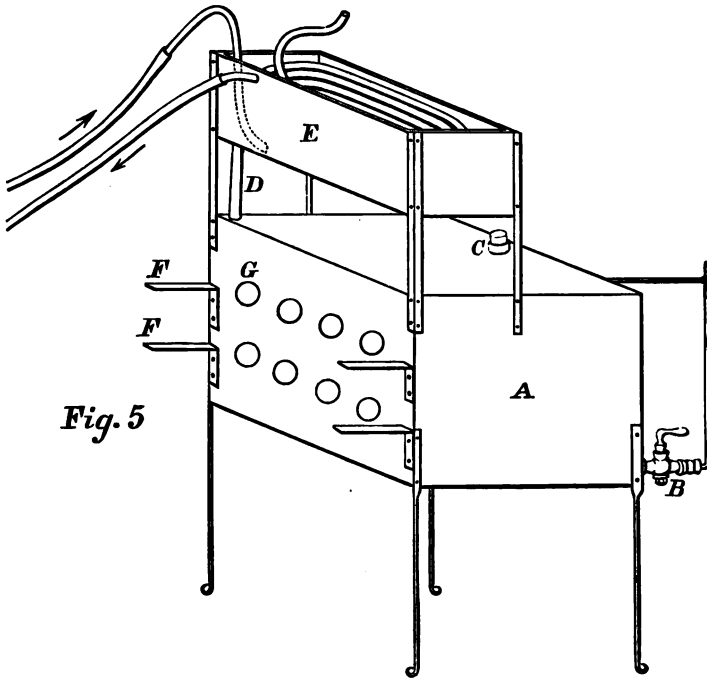


Fig. 5

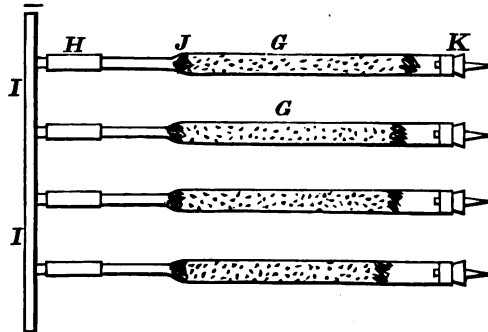


Fig. 6.

material is dried to constant weight. From three to five hours have been found sufficient in most cases. We have practiced replacing the hydrogen in the tubes at the close of the operation by dry air before weighing.

## ALIUQUOTIMETER.

By A. L. WINTON.

This apparatus is made with special reference to the routine work of fertilizer analysis. To determine total phosphoric acid,  $2\frac{1}{2}$  or 5 grams of the phosphate, after ignition with magnesium nitrate, are brought into\* a half-liter flask and dissolved in boiling hydro-

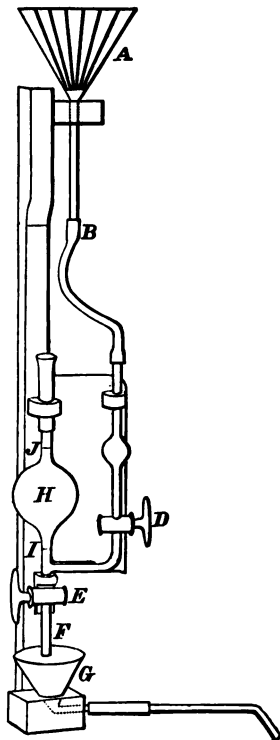


Fig. 7.

chloric or nitric acid. It is then necessary to make the volume of solution 500cc., to pass it through a dry filter and measure off 100cc. for the determination. If the number of determinations is large, these operations are very tedious when hand-pipettes are employed, the least agreeable part of the work being the continued use of the mouth in filling and rinsing the pipette. A fun-

\*Messrs. Whitall & Tatum of N. Y., supply half-liter flasks accurately graduated, in which solutions can be boiled.

nel and a flask are also required for each determination, thus adding considerable to the labor of dish-washing. For accurate work a pipette should never be emptied by blowing into it and should be held perfectly still while the liquid is running out, points which are sometimes disregarded, but which with the apparatus here described do not tax the operator's attention.

In fig. 7, *H* represents a pipette properly graduated to deliver 100cc. when the surface of the liquid falls from the mark *J* to *I* by opening the stop cock *E*.\* Below *I* is a branch tube having a stop cock with  $\frac{1}{8}$ -in. bore, *D*, and a small bulb which prevents bubbles of air from being carried down the tube. To this tube by the rubber at *B* is attached a funnel *A*. The apparatus is mounted on a portable wooden support, shown in the figure all but the flat base,  $12 \times 6 \times 1$  inch.

For use, *D* and *E* being closed, the solution to be measured is poured on a plain filter, contained in the funnel. When the solution has filled the funnel, *D* is opened and the pipette *H* filled. Next *D* is closed and *E* opened, and to rinse the apparatus, the solution is run off through *G* to the sink. *E* is again closed, *D* is opened and the pipette filled to the mark *J*. Next, *D* being closed, 100cc. are drawn off through *F* into the beaker for precipitation. The filter and contents are removed and the same operations are repeated with the next solution. The waste-funnel is mounted in a block of wood with which it is pushed aside when the aliquot is drawn into a beaker.

To secure rapid filtration in the funnel *A*, a number of slender glass rods are disposed radially within it. They may be kept equidistant and in proper position by ligatures of thin platinum wire. Folded filters are very liable to be broken, but might doubtless be used if supported at the vertex by a platinum cone.

#### APPARATUS FOR DETERMINING NITROGEN BY THE METHOD OF KJELDAHL.

BY S. W. JOHNSON.

1. The substance to be analyzed is weighed into long-necked pear-shaped digesting flasks whose transverse diameter is about 3 inches. Ten of these are firmly supported in a portable box or frame of light wood† (not figured) carrying two horizontal shelves

\*Made by E. Greiner, 63 Maiden Lane, New York.

†Devised and constructed by A. L. Winton and H. Lange.

21 inches long, 8 inches wide and 6 inches apart, the lower one having two rows of  $2\frac{1}{4}$  inch holes over which the flasks rest, the upper shelf being divided lengthwise into three sections. Of these, the two outer ones are fixed to the frame; they are 2 inches wide and each has on its inner edge five notches of about 1 inch depth which engage the necks of the flasks. The third movable section, 4 inches wide, when put in place secures the flasks in a nearly vertical position.

2. The sulphuric acid is measured into the digesting flasks by help of the arrangement *a*, *b*, *c* shown at the right in fig. 8.\* The  $\text{H}_2\text{SO}_4$  reservoir *a* of 4 liters capacity is supported on a shelf. It is closed by a rubber stopper through which pass two glass tubes. One of these communicates with the exterior air through an oil vitriol trap to exclude ammonia. The other is a siphon whose short arm (erroneously figured) reaches to the bottom of *a*, and whose long arm is provided with a cock, and connects by a rubber stopper with the measuring cylinder *b*. Except when *b* is in actual use, the upper lateral cock is kept closed. The delivery tube must be rinsed with a little acid just before using to remove any absorbed ammonia. When *b* is not in use, the small beaker *d*, supported by a hinged wire, is brought under *c* to catch the drip. The cylinder *b* is secured to the vertical edge of a fixed wooden support by means of tin-plate clamps and wood-screws.

3. The digestion flasks charged with acid and mercuric oxide are next placed on the lamp stand, fig. 9, which is made of stout sheet iron. The ends as seen in cut, measure 6 inches high, 6 inches wide at top and  $7\frac{1}{2}$  inches at bottom. Each end is made from a piece of iron so large that by turning its edges at right angles and cutting away the overlapping corners, a flange is made 2 inches wide at bottom and 1 inch wide on the top and sides. Each end is notched below to admit the long gas tube which bears the Bunsen burners. An iron sheet 13 inches wide and (for 8 flasks), 37 inches long is bent lengthwise at nearly right angles one inch from one edge and again at about 6 inches from the other edge to form a top, a back and a narrow front to the stand. This piece of metal is finally riveted to the inch flanges of the end pieces above described.

\*By A. L. Winton.

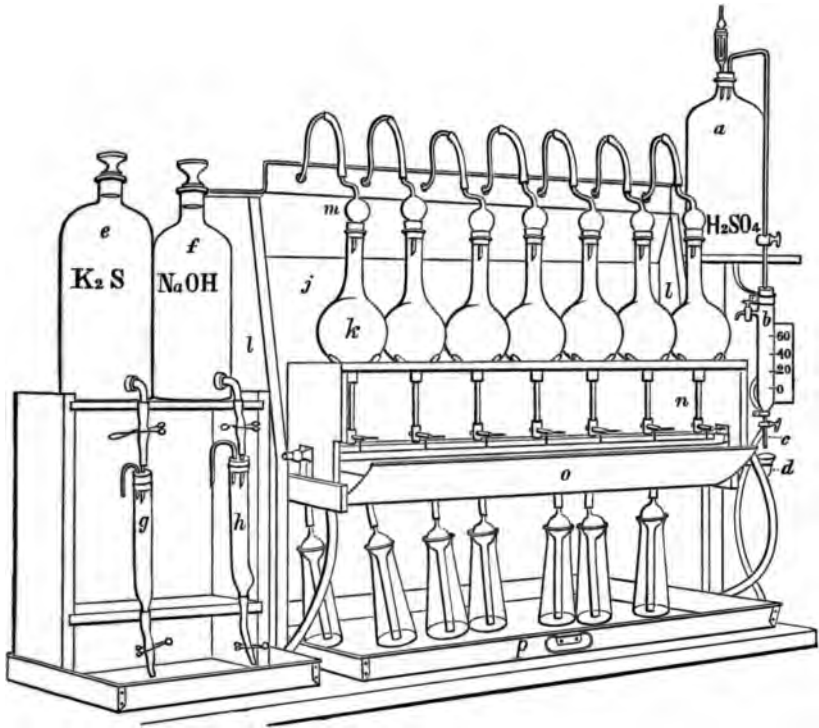


Fig. 8.

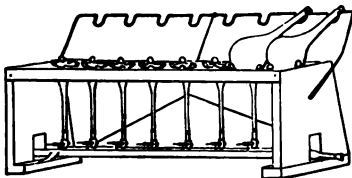


Fig. 9.

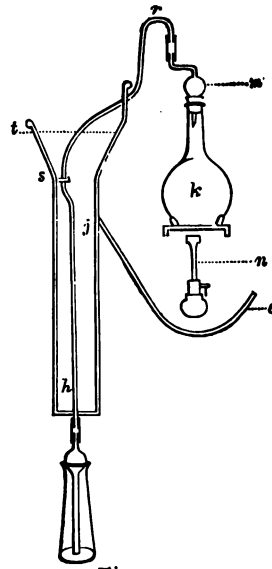


Fig. 10.

Before bending however, 8 holes are cut in the top section as follows: Draw a line 4 inches from and parallel to the edge of the unbent plate, and from centers  $4\frac{1}{2}$  inches apart on this line, describe 8 equidistant circles of  $3\frac{1}{2}$  inches diameter; next mark 12 equidistant points on the circumference of each circle, and from alternate points as centers draw semicircles of  $\frac{5}{8}$  inches radius within the large circles. Now cut away the metal of the large circles except so much as the small semicircles include, and bend upwards at right angles three alternate tongues, thus made, for each aperture. The necks of the flasks are supported at proper inclination by a small iron rod bent and riveted as shown in the figure. The iron ends of the stand are screwed by the bottom flange upon pine strips each  $7\frac{1}{2}$  by 2 by 1 inch, and the gaspipe carrying the lamps is secured to these strips by clamps or bands of sheet iron. The flasks are heated over the naked flame of Bunsen burners arranged like those of the Erlenmeyer combustion furnace. The burners are either widened out funnel-shape at the top and covered with short wire gauze caps, or longer cylindrical gauze caps are supported upon ordinary burners so that the top of the caps is  $\frac{1}{2}$  inch above the burner. By either arrangement the flames may be turned very low without risk of striking down or becoming smoky.

When the digestion is completed and after treatment with permanganate the solutions are transferred to distilling flasks of about 600 cc. capacity, *k*, fig. 8. To each flask is added 25 cc. of  $K_2S$  solution from the bottle *e* by help of the glass measuring cylinder *g*, which swings freely by its rubber connections.\* From *f*\* a slight excess of NaOH solution (50%) is introduced, and after adding a few pieces of granulated zinc and a bit of paraffine to prevent foaming, the flasks are mounted as shown in figures 8 and 10. Each flask is fitted with a rubber stopper carrying a spray-trap *m*†. This is a bulbed tube bent twice at right angles having a diameter of  $\frac{1}{2}$  inch and bore of  $\frac{3}{8}$  inch; the diameter of the bulb is  $1\frac{1}{2}$  inches. The spray-trap is joined by a rubber connector to the block tin-condensing tube *r* fig. 10, which has a bore of  $\frac{1}{8}$  inch and a total length of 32 inches. This condensing tube passes vertically through an open tank made of sheet copper,

\*By A. L. Winton.

†By T. B. Osborne.

*j*, and is firmly soldered into the bottom of the same, but is supported above by simply passing through holes in the upper rim of the tank and in a narrow horizontal shelf at *s*, fig. 10. The dimensions of the tank with 7 condensing tubes are, length 32 inches, depth from *t* 16 inches, width at top 6 inches, at base 3 inches. The tank was widened at the top with a view to its use with ice in hot weather for alcohol estimations, etc. For ammonia-distillations simply, ice is never required, and a tank of much less capacity is sufficient. Cold water is supplied at one end through a siphon, one leg of which is connected with a service pipe, the other reaching to the bottom of the tank. A short efflux tube of  $\frac{1}{2}$  inch bore is soldered into the other end of the tank at the level of *t*. The flasks are heated by gauze-capped Bunsen burners *n* and are supported on an iron shelf quite similar to that represented in fig. 9.

The distillates are received in so-called precipitating jars of about 7 inches height. The tin condensing tubes which project underneath some three inches are joined by rubber connections to bulbed tubes which should be somewhat shorter than shown in figure 8 so as to just dip into the standard acid in the jars. These tubes are of  $\frac{3}{4}$  inch caliber at the widest, except the bulbs which are about  $1\frac{3}{4}$  inches in diameter. The bulbs serve as covers for the jars and assist to prevent loss of their contents either by spitting or regurgitation.

5. The tank when full of water requires a substantial support which consists of two uprights, *ll*, fig. 8, cut from a pine board. Each upright at the base and for half its height is 12 inches wide, at top 6 inches wide and is 27 inches high. At 11 inches from the table the base of the tank rests upon a pine shelf with holes for the projecting tin tubes. This shelf is supported by transverse battens 18 inches long secured to the uprights and which project in front to support the lamp-stand. The uprights are kept in position by means of 4 brass rods of about  $\frac{1}{8}$  inch diameter fitted with screw, nut and washer at each end. These rods traverse the uprights close to the tank, two on its opposite sides below near *h* and two above near the level of *s*. The nuts being screwed on tightly, bind the whole firmly together.

To protect the table and distillate from injury in case a distilling



flask should break, the galvanized iron screen *o*, fig. 10, is employed. The lower part of this is made into a trough by suitable end pieces and at the bottom is connected with the sink by a rubber tube seen at the left in fig. 8.

The spray-traps, devised by Dr. Osborne, are at once effectual and simple, as has been repeatedly proved with distilling flasks more than half full of water, to which 50 cc. of NaOH solution was added, with granulated zinc, boiling as fast as the full heat of the lamps would allow for half an hour. The distillates contained alkali equivalent to but 4-5 one-hundredths of one per cent. of nitrogen reckoned on one gram of substance. When the rate of boiling is not excessive, the error caused by the spray carried over is inappreciable.

A half hour's distillation is sufficient to completely expel ammonia from the distilling flasks and condenser tubes. When in constant use the tank should be emptied once a week and steam blown through the condenser tubes to remove paraffine deposited in them. Glass condensing tubes are objectionable since, as is well known, they always yield more or less alkali to hot water or steam.

In a working day of seven hours one operator with one distilling apparatus and two digestion stands, can make 30 to 35 nitrogen determinations in feeding stuffs. In fertilizers fewer determinations can be made because a longer time is usually consumed in the digestions with sulphuric acid.

#### DRYING OVEN FOR FORAGE SAMPLES.

BY E. H. JENKINS AND S. W. JOHNSON.

A fully representative sample of maize stalks, coarse grasses or other forage plants, can only be secured by gathering a large quantity of the material from all parts of the field, plot or mow. This must then be subdivided and thoroughly intermixed so as to yield finally an average portion not too large to be ground to a fine meal suitable for analysis.

Fresh material containing from 30 to 80 per cent. of water may be cut by machinery or hand into pieces from  $\frac{1}{2}$  to 1 inch long, and, after thorough mixing, a fraction of the whole taken for drying. This is then dried, rough ground, and a weighed fraction of it again taken to be pulverized for analysis. Owing

to the labor involved in handling the bulky material, the temptation is strong to draw samples as small as may be. This always involves danger of making the sample unrepresentative and thus vitiating the results of further work, since without a fair sample the best analysis has little or no value.

A capacious drying apparatus and a mill run by a steam or gas engine makes it possible to handle large samples conveniently and greatly diminishes the risks of sampling. Every agricultural laboratory needs a large drying oven which may be left to the care of laboratory helpers without danger of damage to its contents. It must dry quickly, for slow drying is favorable to loss by fermentation; the heat, however, must not be sufficient to "cook" the samples, i. e., to disintegrate starch grains or coagulate albuminoids.

The oven here described has been in use and has given satisfaction for the last two years. It is built in the basement of the laboratory against a broad chimney-stack which forms its rear wall, and consists of a brick-work base containing the heating apparatus and a wooden superstructure which carries the trays in which the material to be dried is spread. The full details of the carpentry cannot well be given, but are simple and can be readily planned by any practical joiner. The sketch, fig. 11, will give an idea of the construction. The brick base is 32 inches high, 5 feet 6 inches long and 34 inches from front to back, outside measurement. The opening, or fire-door at the end, see fig. 11, is 18 inches wide and is closed by an asbestos board  $\frac{3}{8}$  inch thick, having a wooden base and handle on the outside. The brick-work is 4 inches thick, except at the right of the fire-door, where an 8-inch pier is built. In front two bricks are left out of the lower course and one brick also on the end opposite the fire-door. These are the openings of short brick flues laid on the floor which deliver cold air directly under the smoke pipe within. These openings may be closed with brick when desired. Within this enclosure stands a small cast-iron laundry stove for anthracite or coke, known in trade as "Sweetmeat No. 1." Its widest diameter is about 17 inches and its body is about 16 inches high. To save space the stove without its legs is bedded in mortar on the floor. It is placed as near as possible to the fire-door so that coal can be conveniently supplied

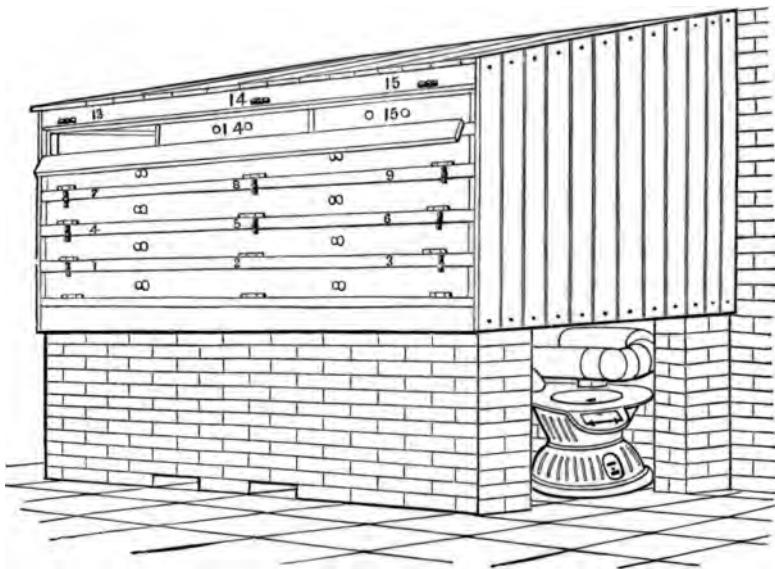


Fig. 11.

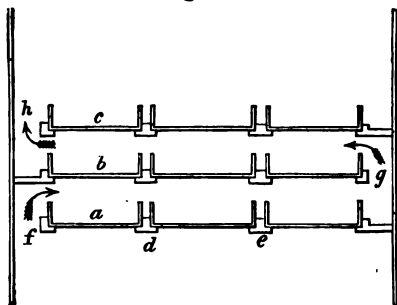


Fig. 12.

and ashes removed. The smoke pipe leading from stove to chimney flue is about 16 feet long and traverses the brick enclosure back and forth four times paralld in lengths (the second and third lengths being under the first and fourth), and enters the flue by a fifth short length near the fire-door. The first, fourth and fifth lengths of pipe are seen in the figure. This pipe has eleven elbows.

A screen of asbestos board  $\frac{3}{8}$  of an inch thick, 4 feet 9 inches long and 34 inches wide is laid over this brick structure, covering the wall at the fire-door end, to protect the wood-work above from

too intense heat. Heated air must therefore pass into the superstructure at the end furthest from the stove. The brick wall so far as not surmounted by the large asbestos board just mentioned is covered by a strip of similar asbestos about 2 inches wider than the wall itself that projects inwards to further protect the wood-work. There thus remains a horizontal opening 3 by 28 inches between the brick-work and the wood-work for the rise of heated air. The asbestos screen is supported at one side by nails driven into the chimney-stack. On the base so prepared stands the dry-house made of wood. Its outside length and width are greater than the base by the thickness of the sheathing, which overlaps the brick. The house is made of  $\frac{7}{8}$  inch pine boards, with exception of four sills, four posts, two plates and two rafters of 2x3 inch scantling. The ends are covered by vertical sheathing nailed to sills and rafters. The posts are further joined, both at front and rear, by six horizontal strips of  $\frac{7}{8}$  inch pine and of 3 inch vertical width, let in flush to the faces of the posts. Through these strips, at the rear, the frame is spiked to the chimney wall. The upper edge of the lower strip is 8 inches above the asbestos screen and the strips above this are 3 inches apart vertically, leaving five interspaces, each of which gives room for three drawers as shown in fig. 11, for which the needful partitions and slides are suitably framed in. At the upper part of the figure, two drawers, Nos. 14 and 15, are shown in place. The drawer-fronts are flush with the outside of the posts and sills. The 3 inch strips between the drawers are not seen in the figure and are covered by  $1\frac{1}{2}$  inch strips nailed over their centers longitudinally, which in the cut are numbered 1 to 9. To the upper edge of each  $1\frac{1}{2}$  inch strip is hinged a  $4\frac{1}{2}$  inch board which serves as a door or lid to shut over the front of three drawers with a bearing on the drawer-frames all around, and these, together with a 7 inch board nailed on at the bottom, make a fairly tight enclosure.

The drawers or trays are each  $20\frac{1}{4}$  inches wide and 34 inches long from front to rear, outside measurement. The drawer-frames are made  $2\frac{1}{2}$  inches deep and the bottoms are galvanized iron netting of  $\frac{1}{4}$  inch mesh secured underneath by  $\frac{3}{8}$  inch strips nailed on through the netting, making a total depth of 3 inches. Two 1 inch auger holes,  $\frac{3}{4}$  inch deep and 3 inches apart, at the middle

of the drawer-front, serves as a "pull". The fifteen trays have an area of over 60 square feet and about  $12\frac{1}{2}$  cubic feet contents.

The interior arrangement is shown in section by fig. 12 (not to scale). Supposing the trays all to be filled with substance to be dried resting on sheets of thin paper that completely cover the netting bottoms, the hot air rising (at the rear end of the horizontal asbestos screen placed between the brick-work and the wood-work) enters *f*, the end-space between the sheathing and the slide on which drawer *a* runs, thence it is made to pass over all the drawers in succession, its course being indicated by the arrows (alternate end spaces, which have a horizontal measurement of 2 by 28 inches, being closed for that purpose) and finally enters the chimney just under the roof of the dry-house by a six inch hole that opens directly into a flue, adjoining and warmed by, the flue which carries off the smoke of the stove. The roof of the dry-house is a movable cover of battened sheathing which rests on the plates and rafters and is kept in position by the sheathing at the ends, and by notches in the rafters which engage the ends of the battens. In drying juicy herbage we find it best to block up the lower edge of the cover an inch or so and let the moisture-laden air escape directly into the room, until the desiccation is well advanced.

Thermometers kept in the trays for hours while fire was burning in the stove, their bulbs being immersed in sand to hold the temperature during observations, gave the following readings in degrees Centigrade :

		12 M.	1 P. M.	3 P. M.	4 P. M.	5 P. M.
Tray No.	1	50°	46°	48°	43°	42°
" "	3	51	50	50	45	44
" "	5	50	46	46	43	41
" "	12	46	40	42	38	42

#### APPARATUS FOR DETERMINING NITRIC ACID.

By T. B. OSBORNE.

This modification of the Schultze-Tiemann apparatus is much more convenient for rapid work than the original. The flask *a*, fig. 13, of about 150 cc. capacity and of glass so thick, that it will sustain the full atmospheric pressure, is provided with a doubly perforated stopper carrying the funnel tube *b*, closed by the pinch-cock *c*. The glass exit tube *d* is joined by stout rubber tubing to the three way tube *e*, as shown in the figure. One branch of this

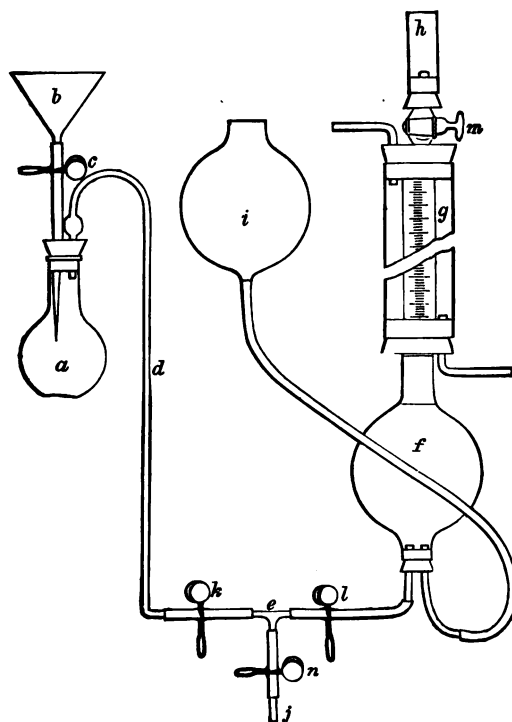


Fig. 13.

tube has a short rubber tube attached which may be closed by the pinchcock *n*. The other branch is connected by glass and rubber tubing with the bulb *f*, which in turn is joined to the 100 cc. burette *g*. This burette is surrounded by a water jacket so that the gas in it may be easily cooled to a constant temperature by a stream of water. The tip of the burette passes through a rubber stopper in a glass tube *h*, which forms a small reservoir for caustic soda solution used to wash the gas at the close of the operation. A second glass tube enters the bottom of the bulb *f*, and is connected by a long rubber tube to the bulb *i*, which contains a ten per cent. caustic soda solution. The substance for analysis is placed in the flask *a*, if necessary enough sodium carbonate is added to make the reaction neutral or alkaline and the flask is then two-thirds filled with freshly boiled water and the stopper inserted. The contents are then boiled down to a small volume,

the steam escaping through *j*, the clamps *k* and *n* being open and *l* closed. In the meantime the burette is filled with freshly boiled caustic soda solution by filling the bulb *i*, and raising it until the solution runs from the burette into *h*. The stopcock *m* is then closed and *i* about half filled with soda solution. When the contents of *a* have been boiled to a small volume the lamp is removed and the clamp *k* is closed and *l* opened. The soda solution will then run out through *j*, filling the tubes; *j* is then closed and *k* opened carefully. The diminishing pressure in *a*, due to cooling, will cause the soda solution to rise in the tube *d*. When it has risen an inch or two, *k* is closed, and by cautiously opening *c* ferrous chloride solution is run from the funnel *b* into *a*, followed by hydrochloric acid. The clamp *c* is then closed and the lamp replaced under *a*. By opening the clamp *k* from time to time the pressure in the flask *a* can be ascertained. As soon as the solution in the tube *d* begins to fall, *k* is left open and the gas from *a* passes through the tubes into *f* and into the burette. In the meantime the bulb *i* is placed in a position below *g* in order to diminish the pressure within the burette. While collecting the gas, water is kept running through the jacket and is allowed to flow over *f*, thereby keeping the solution cool. When the gas has ceased to come off, *h* is filled with the soda solution and by opening *m* the contents are allowed to run slowly into the burette so as to wash the interior surface of the latter and remove any trace of carbonic or hydrochloric acids which it might contain. The cock *m* is then closed, the bulb *i* is raised to bring the surfaces of the solution in the bulb and in the burette to the same level and the volume of gas read. If after a few minutes the reading is unchanged the gas has been cooled sufficiently.

With this apparatus the results obtained have been in every way satisfactory and the time reduced to a minimum. Thirty to forty minutes are commonly sufficient to complete a determination. Further, if it happens that the amount of nitrate present evolves more gas than the burette will hold the boiling may be suspended, the clamp *k* closed and the evolved gas measured. The burette is then filled with soda solution again and the remaining gas collected and measured. By using a flask strong enough to sustain a complete vacuum this can be done easily and without danger.

## THE DISTRIBUTION OF BORACIC ACID AMONG PLANTS.

BY J. S. CALLISON.

Attention was first drawn to the possibility of boracic acid occurring as a normal constituent in certain plants by its discovery in normal California wine.

Baumert\* first drew attention to this in 1885, and his results were confirmed by Rising† and Crampton.‡

These observations were extended to other vines by Baumert,§ Soltsien|| and Ripper.¶

It was shown by Baumert and Ripper, especially, to be almost invariably present in wines of all countries, in the stalks, and even in the wild vine (Soltsien). As Crampton says, "There can no longer be any question, therefore, in view of this mass of evidence, that boracic acid is a normal and frequently occurring constituent of the grape plant." He then asks the question, if boracic is so universal a constituent of the Grape plant, why not of other plants as well? In answering this question he examined certain plants, as the peach, watermelon, apples, sugar-beet and sugar-cane. Thinking this distribution of boracic acid to be a question of decided importance, I have extended the examination, to many other ashes than those mentioned by Crampton, coming from other classes of plants than fruits, though including also some of the fruits.

The results of my work have confirmed the conclusions that boracic acid is very widely distributed in the vegetable kingdom, and that there seems to be a power of selection on the part of the plants, some having no affinity for and not taking up the boracic acid, though growing on the same soil from which other plants absorb it. We are forced to the belief that it is contained in the soil and that the plants draw it from that source, yet in no case could I detect its presence in the soil, and in no well water examined could I get a test for it. It is easily possible that other waters might contain it. It would be of great interest to extend

\*Landw. Versuchstat. **33**, 39-88.

†Report of Sixth Viticultural Convention, 1888.

‡Amer. Chem. Journal, Vol. II, 227.

§Zeitschrift für Naturwissenschaften, 1887, and Ber. d. deutsch. Chem. Ges. **21**, 3290.

¶Pharmaceutische Zeitung **33**, No. 42, p. 312.

¶Weinbau und Weinhandel: Organ des deutschen Weinbauvereins No. 36, 1888.



this examination of natural waters so as to see whether the boracic acid in the soil is in a soluble form or not. It may be present in a form soluble in plant solvents and insoluble in natural waters. Of course, it is possible, also, that it is present in such great dilution that the amount of water evaporated failed to give the qualitative tests. My examination of different fertilizing materials revealed the fact that several of the commonest contained boracic acid in appreciable amounts, and hence, by this means, it is being constantly added to soil under cultivation.

Of course stable manure, coming from grain and straw, restores to the soil the boracic acid contained in these.

A further important fact brought out by this research is that every sample of caustic alkali examined contained boracic acid. These samples were from the best known manufacturers, and were marked chemically pure. As these alkalies, especially potassium hydroxide, are used in most of the methods for determining boracic acid, it is manifestly of great importance to secure them free from it as an impurity. I think it possible that the boracic acid in these samples, or at least in some of them, may have come from the glaze of vessels used in their manufacture or from the bottles containing them.

The method of testing was that used by Meisell for the detection of boracic acid in milk.\* About one gram of the ash was treated with strong hydrochloric acid and boiled a few minutes to insure solution. It was then filtered from the unburnt carbon, insoluble silica, etc. The filtrate was evaporated to dryness on a sand-bath and the heat continued until the excess of acid was driven off and the residue assumed a white appearance. This was then moistened with very dilute hydrochloric acid (1 : 100), a few drops of tincture of turmeric were added, and the entire mass dried down on a water-bath. The appearance of the cherry-red or cinnabar-red color was taken as an evidence of boracic acid. The residue was then used for the flame tests. This was made by placing a part of it upon a strip of platinum, moistening with alcohol and igniting. The green flame flashes, best observed by blowing out and relighting the alcohol, were regarded as confirmatory of the turmeric tests. The flame test is, however, not so delicate as the latter, as has also been observed by Crampton.

\*König's Nahrungsmittel, 2, 250.

The relative and absolute delicacy of these tests was also approximately determined. The flame reaction was still clear with .0001 gm. of boracic acid, but could not be gotten with .001 gm. This latter amount gave the color reaction, but .0001 gm. failed to give it.

These figures apply, of course, only to boracic acid treated under like circumstances to the ash. 10 cc. of a solution of boracic acid of known strength was evaporated in a small porcelain dish and the residue manipulated exactly as in Meisell's test.

The porcelain dishes used in this research, and other apparatus where the presence of boracic acid might be suspected, were carefully tested and shown free from anything that could conflict with the tests.

The appended table gives the substances examined and the results of the tests. In many cases the tests were carefully repeated to insure accuracy. The specimens were chosen so as to represent as many different classes of plants as possible. In the case of caustic alkalies the evaporation and testing were done in platinum vessels.

The experiments with various chemicals, pure and commercial, were begun with the idea of seeing whether those which might have come from some plant source, contained this substance so generally present in the plants themselves. The caustic alkalies were examined with a view to their use in the quantitative determination of boracic acid. Some other chemicals, as ferric oxide, were examined to see if they would in any way interfere with the test when present.

The table which follows will need no further explanation. I wish to express my obligations to Dr. F. P. Venable for his guidance and supervision of my work in this research.

#### *Fruits.*

No.	Common Name.	Botanical Name.	Flame Reaction.	Color Reaction.
1	Fig, green	Ficus Carica	Yes (faint)	Yes
2	leaves		No	No
3	branches		Yes	Yes
4	Persimmon, green	Diospyros Virginiana	Yes (faint)	Yes
5	leaves		No	No
6	Pear, branches	Pyrus Communis	Yes (faint)	Yes
7	leaves		Yes	Yes

8	Apple, pulp	Malus	Yes (faint)	Yes
	seed		Yes (faint)	Yes (faint)
9	Peach, branches	Prunus Communis	Yes (faint)	Yes
10	leaves		Yes	Yes
11	HoneyLocust, pods	Gleditschia triacanthos	Yes	Yes
12	Lemon, pulp	Citrus Limonum	No	Yes
13	rind		Yes	Yes
14	Orange, pulp	Citrus Aurantium	Yes	Yes
15	rind		Yes (faint)	Yes
16	seed		No	Yes
17	Banana	Musa Sapientum	No	Yes
18	Dates, dried		Yes (faint)	Yes (faint)
19	seed		Yes (faint)	Yes (faint)
20	Cherry, branches	Prunus Ceracus	No	No
21	leaves		Yes (veryfaint)	Yes (faint)
22	Cocoanut, shell	Coco Nucifera	No	Yes (faint)
23	Raspberry, leaves	Rubus Strigosus	No	Yes
24	Blackberry, stalk	Rubus Villosus	No	Yes
25	leaves		No	Yes
26	Strawberry, leaves	Fragaria Vesca	Yes	Yes
27	Grape, Concord, leaves	Vitis Labrusca	Yes	Yes
28	stalk		Yes	Yes
29	Wild, leaves	Vitis Cordifolia	No	Yes
30	stalk		No	Yes
<i>Vegetables and Grains.</i>				
31	Pea	Pisum Arvense	Yes	Yes
32	Beet, root	Beta Vulgaris	Yes	Yes
33	leaves		Yes	Yes
34	Salsify, root	FragopogonPorrifolium	Yes(veryfaint)	Yes (faint)
35	leaves		Yes	Yes
36	Celery	Apium Graveolens	Yes	Yes
37	Wheat, grain	Triticum Vulgare	Yes (faint)	Yes
38	green stalk		Yes	Yes
39	Oats, grain	Avena Sativa	No	Yes (faint)
40	green stalk		Yes	Yes
41	Corn, grain	Zea Mays	No	No
42	cob		No	Yes (very faint)
43	stalk		No	No
44	blades		No	No
45	Maple, branches	Acer Rubrum	Yes	Yes
46	leaves		Yes	Yes
47	Willow, branches	Salix Nigra	Yes	Yes
48	Mulberry, wood	Morus rubra	Yes	Yes (faint)
49	bark		No	No

50	Walnut, branches	Juglans Nigra	Yes	Yes
51	Sumach, berries	Rhus copallina	Yes	Yes
52	branches		Yes	Yes
53	Pine, long leaf, branches	Pinus Australis	Yes	Yes
54	leaves		Yes (faint)	Yes
55	short leaf branches	Pinus Mitis	Yes	Yes
56	leaves		Yes	Yes
57	Dogwood, branches	Cornus Florida	Yes (faint)	Yes
58	Cedar, branches	Juniperus Virginiana	Yes	Yes
59	leaves		Yes	Yes
60	Oak, branches	Quercus alba	Yes (faint)	Yes
61	leaves		Yes	Yes
62	acorn		Yes (faint)	Yes
63	Sycamore, branches	Plantanus Occidentalia	Yes	Yes
64	Elm, branches	Ulmus	Yes	Yes
65	Black How, branches	Viburnum Prunifolium	Yes	Yes
66	fruit		Yes	Yes
67	Hickory, branches	Carpa	Yes	Yes
68	nut		Yes (faint)	Yes (faint)
69	Magnolia, branches	Magnolia Grandiflora	Yes	Yes
70	leaves		Yes	Yes
71	Holly, branches	Ilex Opaca	Yes	Yes
72	leaves		Yes	Yes
73	berries		Yes	Yes
74	Paulonia, buds	Paulonia imperialis	Yes	Yes
75	pods		Yes	Yes
76	Osage Orange	Maclura Aurautiaca	Yes (faint)	Yes

*Miscellaneous Plants.*

77	Tobacco, stalk	Nicotiana Tobacum	Yes	Yes
78	leaves		Yes	Yes
79	Cotton, lint	Gossypium herbaceum	Yes(veryfaint)	Yes (very faint)
80	seed		Yes(veryfaint)	Yes
81	stalk		Yes	Yes
82	AzaleaIndica, leaves	Azalia Indica	No	Yes (faint)
83	root		No	No
84	Chrysanthemum, stalk	Chrysanthemum Pompone	No	Yes (faint)
85	flower		No	Yes (faint)
123	Rose, branches		Yes	Yes
86	Bamboo	Smilax Rotundifolium	Yes	Yes
87	Sorrel	Oxalis Stricta	Yes	Yes
88	Lucerne	Medicago Sativa	Yes	Yes

89	Clover, red	Trifolium Pratense	Yes	Yes
90	white	Trifolium Repens	Yes	Yes
91	Orchard Grass	Dactylis Glomerata	Yes (faint)	Yes
92	Blue Grass	Poa Compressa	Yes	Yes

*Soils, Waters and Fertilizers.*

No.	Common Name.	Remarks	Flame Reaction.	Color Reaction.
93	Alluvial	2 kilos taken	No	No
94	Sandy, rich	" "	No	No
95	Sandy, poor	" "	No	No
96	Red Clay		No	No
97	Well Water, No. 1	48 liters taken	No	No
98	No. 2	56 " "	No	No
99	Water from small stream	36 " "	No	No
100	Bone and Peruvian Guano		Yes	Yes
101	Peruvian Guano		Yes (faint)	Yes
102	Bone Ash		No	No
103	Sodium Nitrate	Crude	No	No
104	Muriate of Potash	From Stassfurt	Yes	Yes
124	Kainite	For Fertilizers	No	Yes
125	Kelp		Yes	Yes

*Chemicals.*

105	Potassium Nitrate	C. P.	No	No
106	Potas'm Carbonate	C. P.	No	No
107	Potassium Chlorate	C. P.	No	No
108	Potas'm Carbonate	Commercial	Yes	Yes
109	Potassium Sulphate	C. P.	No	No
110	Sodium Nitrate	C. P.	No	No
111	Sodium Carbonate	C. P.	No	No
112	Calcium Carbonate	C. P.	No	No
113	Ferric Oxide		No	No
114	Concentrated Lye	Commercial	No	Yes (faint)
115	Potas'm Carbonate	Pearlash	No	No
116	Potas'm Hydroxide	C. P., Trommsdorf	Yes	Yes
117	"	" by alcohol, Marquart	No	Yes
118	"	" by baryta, Schuchardt	No	Yes
119	"	" Eimer & Amend	No	Yes
120	"	" C. P., free from $Al_2O_3$ , $SiO_2$ and $SO_3$ , Eimer & Amend	No	Yes
121	Sodium Hydroxide	C. P.	Very faint	Yes
122	"	"	No	Yes (very faint)
126	Ammon'm	"	No	No

## ON THE OCCURRENCE OF BORACIC ACID AS AN IMPURITY IN CAUSTIC ALKALIES.

BY F. P. VENABLE AND J. S. CALLISON.

In the course of a research upon the distribution of boracic acid in the ashes of plants, it was decided to make some quantitative estimations of the boracic acid present. The reagents to be used were first themselves tested for boracic acid, and, much to our surprise, no sample of the caustic alkalies could be procured free from it. Specimens coming from some of the most noted manufacturers, Schuchardt, Marquart, and Trommsdorff, purified by alcohol or by baryta, were found to contain boracic acid, and sometimes in decidedly appreciable amounts. No quantitative determination has been made, but, judging from the known delicacy of the qualitative tests, the amount must have often exceeded 0.1 per cent., and was probably much greater.

As the caustic alkalies, especially potassium hydroxide, are frequently used in the methods for the quantitative determinations of boracic acid,\* this presence of it as an impurity may be a serious source of error. The knowledge of it is important on other grounds as well.

UNIVERSITY OF NORTH CAROLINA,  
May, 1890.

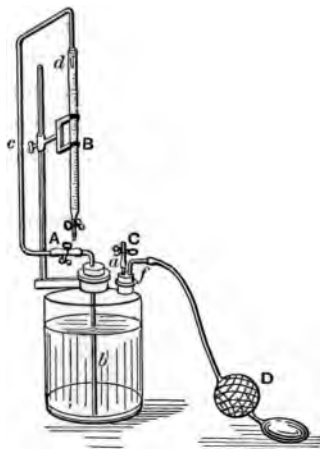
\*See for instance, Morse & Burton, Amer. Chem. Jour. X, 154. Ztschr. anal. Chem. 25, 202.

# ABSTRACTS.

## APPARATUS AND REAGENTS.

**A New Titration Apparatus.**—Victor Hölbling, *Zeitschr. anal. Chem.* **28**, 431.

The apparatus shown in the accompanying cut is claimed by the author to be new in several respects, and to be particularly useful when a number of titrations are to be made in rapid succession with the same solution. The construction of the apparatus is evident from the cut, and the mode of using it is very simple. Open the pinch-cock *A*, and by means of the bulb *D* pump air into the bottle *F*. This forces the liquid through *c* into the burette *B*, the air escaping from the burette through a small channel cut in the side of the cork which is in the upper end of the burette. As soon as the burette is filled so that the point of the tube *d* is below the surface of the liquid, close the pinch-cock *A* and open *C*. This allows the air in *F* to escape until it is at the normal pressure. Now open *A* again, and *c*, acting as a siphon, will draw the excess of liquid from the burette, and as the point *d* is exactly at the zero mark of the burette, the latter is now ready for use.



A. A. B.

**Centrifugal Action in Laboratory Work.**—H. Leffman and W. Beam, *The Analyst* **15**, 25. The authors have used this process in several laboratory manipulations with the following results:

A sample of slightly turbid urine was tried, with a view of

obtaining the suspended matter for microscopical examination. A rotation of about one minute, at a speed of 16 revolutions per second, produced a clear liquid with the sediment packed in one end of the tube so tightly that the liquid could easily be removed by decantation. Equally satisfactory results were obtained with recently precipitated barium sulphate, calcium oxalate, prussian blue, etc. They have also found that the emulsion which chloroform sometimes forms with aqueous solutions is at once separated.

The machine used was modelled after the lactocrite, such as used in creameries, and the essential feature was that the tube carriers were connected by a hinge to a vertical revolving rod. This permits the tubes to hang upright when at rest and assuming a horizontal position only when in rapid rotation which makes the closing of the tubes unnecessary.

S. C.

**The Concentration of Reagents.**—R. Blochmann, Ber. 23, 31, notes the wide differences in practice in making up solutions of reagents. Without any apparent reason some solutions are made up 1:5, 1:10, 1:15, 1:20, etc., by one chemist, while another will make up the same solutions 1:6, 1:12, 1:24, etc., and a third 1:2, 1:3, 1:4, 1:8, etc. He recommends that solutions be so made up that the volume shall bear some simple relation to the amount of contained salt on the basis of Mohr's normal solution system. It is not necessary that the solutions should be made up with great care; for most purposes it is sufficient if the actual content of salt be *nearly* that described by the label. In many cases this may be done conveniently by diluting saturated solutions of salts to the requisite degree with water.

A few substances, such as lime water, bromine water, etc., cannot be made up in this way because of their lack of solubility, and with a few others, as, for example, concentrated sulphuric acid, it is not practicable.

Some of the solutions proposed by the author are the following:

*1. Concentrated Acids.*

	Sp. gr.	Per centage.	1 L. contains
Concentrated Hydrochloric Acid, 1.160	31.8	369 gms.=about 10 HCl.	
Concentrated Nitric Acid . . . . 1.305	48.1	628 gms.=about 10 HNO <sub>3</sub>	
Concentrated Sulphuric Acid . . 1.840	96.0	1767 gms.=about 36 $\frac{\text{H}_2\text{SO}_4}{2}$	



*2. Normal Solutions.*(a)  $\frac{2}{1}$  normal.

	Percentage Weight.
Hydrochloric Acid . . . . .	7.1
Nitric Acid . . . . .	11.8
Sulphuric Acid . . . . .	9.2
Acetic Acid . . . . .	11.8
Oxalic Acid . . . . .	12.3
Tartaric Acid . . . . .	14.1
Potassium Hydroxide . . . . .	10.3
Sodium Hydroxide . . . . .	7.4
Ammonia . . . . .	3.5
Ammonium Sulphide . . . . .	6.8
Ammonium Chloride . . . . .	10.4
Ammonium Carbonate . . . . .	9.4
Sodium Carbonate . . . . .	9.6
Sodium Acetate Crystals . . . . .	25.2

(b)  $\frac{1}{1}$  normal.

Barium Chloride Crystals . . . . .	11.2
Calcium Chloride Crystals . . . . .	10.5
Ferric Chloride . . . . .	5.2
Potassium Sulphate . . . . .	8.1
Magnesium Sulphate Crystals . . . . .	11.6
Copper Sulphate Crystals . . . . .	11.6
Di Sodium Phosphate Crystals . . . . .	11.4
Lead Acetate Crystals . . . . .	16.9
Potassium Chromate . . . . .	9.0
Potassium Ferrocyanide Crystals . . . . .	10.0

(c)  $\frac{1}{2}$  normal.

Platinic Chloride . . . . .	8.0
Silver Nitrate . . . . .	8.0
Mercuric Chloride . . . . .	6.4
Barium Nitrate . . . . .	6.2

*3. Oxidizing and Reducing Reagents.*(1 liter =  $\frac{+}{2}$  O = 8 gms. oxygen.)

Percentage Weight.	1 Liter Contains
Potassium Dichromate . . . . . 4.7	$\frac{1}{6}$ $K_2Cr_2O_7$ = 49.0 gms.
Sodium Hypochlorite . . . . . 3.7	$\frac{1}{2}$ $NaClO$ = 37.2 "
Sodium Nitrite . . . . . 4.2	$\frac{1}{2}$ $KNO_2$ = 42.5 "
Stannous Chloride . . . . . 10.5	$\frac{1}{2}$ $SnCl_2 \cdot 2aq$ = 112.5 "

4. *Saturated Solutions.*

	Percentage Weight at 15° C.	One Liter Normal Solution corresponds to
Sulphuretted Hydrogen Water, 0.48 H <sub>2</sub> S		3.5 liters
Baryta Water . . . . .	5.95 Ba(OH) <sub>2</sub> , 8aq	2.6 "
Lime Water . . . . .	0.13 CaO	21.5 "
Gypsum Water . . . . .	0.26 CaSO <sub>4</sub> , 2aq	33.0 "
Bromine Water . . . . .	3.23 Br.	2.5 " ( $\frac{0}{2}$ )

E. H.

**Vanadium in Caustic Potash.**—Edgar F. Smith, Chem. News 61, 20 (from the "Journal of the Franklin Institute"). Dr. Smith found, while using the ordinary stick caustic potash, indications of the presence of vanadium. To confirm his opinion, three pounds of stick potash in warm aqueous solution were saturated with sulphuretted hydrogen, heat was applied for several hours longer, the liquid meanwhile taking on a yellow to a deep red color. Hydrochloric acid was now added to acidify the solution, and the separated sulphur was quite dark in color. The free sulphur was extracted from the residue, after filtration and washing, by carbon disulphide. The chocolate colored mass remaining was nearly all soluble in yellow ammonium sulphide, and was precipitated by dilute acid. Washing this precipitate and treating with carbon disulphide, a crystalline mass remained. Tests for Vanadium were then made with this product. The phosphorus bead test was satisfactory. A test used by Dr. Walz (American Chemist 6, 453), in detecting minute quantities of vanadium in American magnetites, was made as follows: A portion of the ignited residue was dissolved in a drop of sulphuric acid free from iron. 1 cc. of water was added and one or two drops of a dilute potassium ferrocyanide solution produced a fine green coloration in the liquid. The remainder of the ignited residue was dissolved in nitric acid, and a large piece of ammonium chloride added to the ammoniacal liquid, when, on standing over night, crystals of ammonium vanadate separated, which gave the characteristic reactions for vanadium compounds. The vanadium sulphide at first obtained was freed from silver and iron with which it was contaminated, that the reaction might be unquestionable. Three pounds of caustic potash gave about .5 gm. of the impure sulphide.

A. H. W.

**An Investigation of Sodium Carbonate.**—R. Kissling, *Ztschr. angew. Chem.* 1889, 332.

The author finds that if carbonate of sodium is heated above  $150^{\circ}$ , part of the carbonic acid is driven off, and the residue, when dissolved in water, gives decided reaction for hydrate.

J. E. W.

**The Use of Peroxide of Hydrogen in Preparing Oxygen with the Kipp Apparatus.**—A. Baumann, *Ztschr. angew. Chem.* 1890, 79.

The middle bulb of the apparatus is to be filled with pyrolusite in pieces the size of a pea. Commercial hydrogen peroxide is used with an addition of 150 cc. of sulphuric acid to the liter.

The author claims a very pure product, and a flow of gas as steady as when zinc and sulphuric acid are used in preparing hydrogen.

J. E. W.

**Determination of the Specific Gravity of Sirups and Similar Viscous Liquids.**—A. Genieser, *Ztschr. angew. Chem.* 1890, 44.

The sirup, after being strained, is weighed in a picnometer, which should be about two-thirds filled. This is placed in a bath, whose boiling point is higher than that of the sirup, and the temperature raised to the boiling point and kept so for an instant, when the picnometer is taken from the bath and allowed to cool to  $17.5^{\circ}$ . By this any air that was contained in the liquid is expelled. The picnometer is then filled with water at  $17.5^{\circ}$  and weighed. By knowing the weight of the picnometer filled with water at  $17.5^{\circ}$ , the specific gravity may be calculated in the usual way.

J. E. W.

**The Graduation of Tubes for Gasometric Apparatus.**—M. Berthelot, *Bull. soc. Chim.*, 49, 959. The tube to be graduated is exactly filled with pure mercury, free from bubbles of air, and the open end closed by pressing a smooth glass plate upon the convex surface of the mercury, thus insuring the complete filling of the tube. The entire apparatus is then carefully weighed and the tube placed in a vertical position with the plate-covered end downward. The glass plate is then slightly lowered at one side and a small amount of mercury allowed to run out. The plate is then replaced and the graduation corresponding to the

level of the mercury in the tube ascertained by means of a lens. The weight of the mercury drawn out is now taken, either by determining the loss in weight of the whole apparatus, or by weighing the amount removed direct. This weight, divided by the density of the mercury at the temperature of the experiment, gives the volume of the space remaining in the tube. Eight or ten of these operations can be made in an hour upon the same tube and a table of corrections for the graduation of the tube thus obtained. It is better, however, to have the tube graduated originally in this manner by the maker.

I. A. P.

**A Brief Summary on Practical Manipulation.**—H. N. Warren, Chem. News 61, 63 and 100.

*Precipitation.*—To prevent imperfect filtration, as in the case of finely divided precipitates, such as barium sulphate, keep both the reagent and the solution containing the sulphate at a high temperature and add a few drops of an ethereal solution of pyroxylin and mix well by stirring. The pyroxylin is set free, and mixing with the precipitate, permits an immediate filtration. The addition of finely powdered glass, in making a basic acetate separation, will, at the boiling temperature, cause the precipitate to subside. In making pharmaceutical preparations, such as Tinctura rhei of the British Pharmacopœia, digestion with a small quantity of egg albumen caused it to be readily filtered through ordinary filter paper. Paper pulp also has the power of retaining very perfectly finely divided substances.

*Incineration.*—In determining total ash, as in the analysis of beet-sugar, the addition of a small quantity of  $H_2SO_4$  is required to convert the inorganic salts into sulphates and thus render them less fusible, the proper deduction being made. To overcome the imperfect combustion of carbon when in contact with phosphates, the author uses a plug of gun-cotton, omitting altogether a filter paper.

*Precipitation Retarded.*—Glass-wool may be used in cases where incautious filtration through organic membranes of strong acid liquors might form organic salts which would retard the precipitation of the metals.

*Reading of Definite Quantities from Measured Flasks.*—The

addition of a single drop of alcohol will dispel the froth or air-bubbles which frequently prevent an accurate reading.

*Disintegration.*—A smooth iron plate, and a large flat-headed hammer, giving to the latter a rotary motion, so as to bring the same particles constantly under its influence, serve as an easy method for the pulverization of minerals.

*Casting and Moulding.*—For metals whose melting points are not higher than zinc, a convenient test-mould is made by wrapping around an ordinary lead-pencil, several thicknesses of writing paper, closing the end by a cork, and immersing the mould to its extremity in dry sand, when the core is withdrawn and the molten metal cast. For copper, iron, etc., asbestos sheeting is substituted.

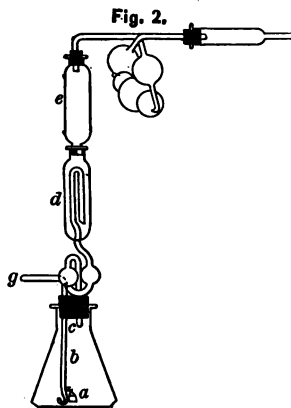
*Combustion Tubing.*—To prevent breakage, a thin strip of asbestos is placed underneath the glass.

*Unsuspected Impurity of Acids.*—Attention is called to the fact that selenium has often been detected in a so called pure nitric acid and when used for parting gold a serious error might result from the use of such contaminated acid.

A. H. W.

### Apparatus for the Direct Determination of Carbon Dioxide.

—O. Ostersetzer, Ztschr. anal. Chem. 27, 27. *b* has a capacity of 70 cc. and contains dilute hydrochloric acid. *g* is connected during the analysis with a potash bulb to free the air passing into the flask from  $\text{CO}_2$ . *d* contains concentrated sulphuric acid and *e* pumice stone saturated with copper sulphate to take up any vapor of hydrochloric acid. The carbon dioxide is then absorbed in the potash bulb, to which a soda-lime tube is attached. The substance is weighed into the small glass basket *a* which is immersed in the acid by pushing the tube *g* downwards.



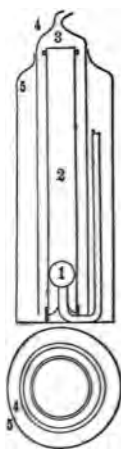
**The Use of Normal Ammonia Solution.** R. Rempel, Ztschr. angew Chem, 1889, 331. The author shows by the results he ob-

tained that there is a loss of ammonia when an open vessel is used to titrate into.

He recommends the use of an Erlenmeyer flask, a solution not higher than  $\frac{1}{2}$  normal, and cautions the operator against titrating into hot solutions.

His figures show lower results when Methyl orange was used as an indicator than by the use of litmus solution. J. E. W.

**Sulphuretted Hydrogen Generator.**—W. Oakes Kibble, Chem. News 61, 105.



The apparatus consists of an inner tube with studs holding a glass ball loosely fitting, which supports the ferrous sulphide. The bottom is closed and a tube sealed in preventing escape of particles of sulphide. An outer-tube fits over this drawn out for attachment of rubber tube and tap or pinch-cock. A thin glass tube reaches from the trap into which it fits, three-quarters of the way up the outside. A rubber collar at the bottom and band at the top of the inner tube prevent jarring. The whole is placed in an ordinary broad-necked bottle, which holds the acid, and a rubber ring is fitted three-quarters of the way around in the neck to prevent the outer cylinder from rising.

To use the jar, it is filled three-fourths full of dilute acid, then the inner tube filled with sulphide is put in place, the outer tube is slipped over it, and the tap or pinch-cock is closed. The acid enters, acts on the sulphide, generating  $H_2S$ , which, filling the tubes, leaves the sulphide practically dry. As the gas is used, fresh acid enters and generates a fresh supply. A. H. W.

## WATER ANALYSIS.

**A New Method of Estimating the Oxygen Dissolved in Water.**—John C. Thresh, Jour. Chem. Soc. 1890, 185.

The following solutions are used :

1. A solution of sodium nitrite and potassium iodide.
2. Dilute sulphuric acid.
3. A solution of starch.
4. A solution of

sodium thiosulphate containing 7.75 gms. in one liter each cc. of which corresponds to 0.25 milligram of oxygen.

The apparatus used consists of a wide-mouth bottle fitted with a caoutchouc stopper having four perforations. Through two of these openings pass glass tubes by means of which coal gas may be passed through the bottle. A separatory funnel to admit the measured quantity of water to be tested and a graduated burette for the sodium thiosulphate solution are fitted in the other openings. This completes the apparatus and is shown in a cut.

The burette and separatory funnel are filled and one cc. each of solution of sodium nitrite and potassium iodide, and dilute sulphuric acid are added by means of a pipette and the stopper quickly replaced. The vessel is then shaken slightly and allowed to remain fifteen minutes, after which a current of coal gas is passed through the bottle. The water is now allowed to flow into the bottle, the surface being protected against the air by the insertion of a perforated cork through which passes a stream of coal gas. Thiosulphate solution is now run in from the burette until the color of iodine almost disappears, at which point one cc. of starch solution is added from the separatory funnel which previously held the water. Thiosulphate is then added until the blue color disappears, allowed to stand two minutes and then enough added to decolorize the blue color which reappears.

"The number of cc. used will represent  $a$ , the oxygen dissolved in the water examined,  $+b$  the nitrite in 1 cc. of solution used, and the oxygen in the acid and starch solution  $+c$ , a portion of the dissolved oxygen in the volumetric solution." The value of  $b$  and  $c$  are to be determined.

By using 5 cc. of nitrite solution, dilute sulphuric acid solution and starch solution and titrating without water and dividing the result by five,  $b$  may be obtained.

The author directs to find the value of  $c$  as follows :

"This correction is a comparatively small one and admits of determination with sufficient accuracy if we assume that the thiosulphate solution normally contains as much dissolved oxygen as distilled water saturated at the same temperature. Complete a determination as above described, then remove the stoppered tube, and insert a tube similar to that attached to the burette, and drop

in from 10 to 20 cc. of saturated distilled water exactly as the thiosulphate is dropped in. Allow to stand a few minutes and titrate. One-tenth or one-twentieth of the volumetric solution used, according to the number of cc. of water added, will represent the correction for each cc. of volumetric solution used. Call this value  $d$ .

Let  $e$  be the number of cc. of thiosulphate used in an actual determination of the amount of oxygen in a sample of water.

$f$  = the capacity in cc. of the tube employed — 2 cc., the volume of reagents added.

$g$  = the amount of oxygen in milligrams dissolved in 1 liter of the water ;

$$\text{then } g = \frac{1000}{4f}(e - b - ed).$$

With a tube made to hold exactly 250 cc., the most convenient quantity to use  $\frac{1000}{4f}$  becomes unity and

$$g = e - b - ed."$$

C. W. M.

### The Alleged Sterilization of River Water by Mine Water.

A. A. Breneman, Jour. Am. Chem. Soc. 12, 12.

During an epidemic of typhoid fever which occurred in Wilkes-Barre, in the summer of 1889 ; attention was directed to the water as being the cause of the trouble. The author gives the results, in the accompanying table of a bacteriological, and chemical examination of three samples of water taken.

1. From the Susquehanna River at the intake of the Wilkes-Barre Water Co.

2. From the mouth of the shaft of the Hollenback coal mine, the drainage from which runs into the river above Wilkes-Barre.

3. (For comparison only). From Mine No. 3, of A. Pardee & Co., at a depth of 300 feet below the surface.

#### Chemical Examination.

Grains per U. S. Gallon.

	Total Acid. SO <sub>3</sub>	Free Sulphuric Acid. H <sub>2</sub> SO <sub>4</sub>	Ferric Oxide. Fe <sub>2</sub> O <sub>3</sub>	Lime.	Magnesia.	Silica.
1	1.00	.00	.71	1.88*	.46†	. .
2	51.16	15.59	12.23	8.21	4.09	2.50
3	127.30	20.85	65.40	2.55	4.27	2.70

\*Equivalent to 2.1 grains CaCO<sub>3</sub> or 1.7 grains CaSO<sub>4</sub>

†Equivalent to 0.96 grains MgCO<sub>3</sub>



A bacteriological examination was then made by Dr. H. Biggs, of Bellevue College Hospital. Dr. Biggs found from 400 to 500 germs per cc. of at least fourteen different species in samples No. 1 and 2. In conclusion, the author states that no effective sterilization of a large stream of water can result from the small contributions made to it by mine drainage.

F. R. B.

**The Manganese Waters of Excelsior Springs.**—W. P. Mason, Chem. News 61, 123.

Excelsior Springs, a small town about thirty miles northeast of Kansas City, Mo., is noted for the therapeutic value of its chalybeate waters. In only seven of the sixty-two springs in the United States in which manganese is reported does the amount of the metal equal or exceed that in the Excelsior Springs, and in all but two of these (and these doubtful) the element is present as sulphate or chloride, while in the Excelsior water it occurs as carbonate only, a form readily adapting it for medicinal administration. The analysis of Prof. Mason is as follows:

MnCO <sub>3</sub> . . . . .	9.41	parts per million
Al <sub>2</sub> O <sub>3</sub> . . . . .	2.10	" "
SiO <sub>2</sub> . . . . .	12.00	" "
K <sub>2</sub> SO <sub>4</sub> . . . . .	4.86	" "
NaCl . . . . .	17.60	" "
FeCO <sub>3</sub> . . . . .	23.43	" "
CaCO <sub>3</sub> . . . . .	362.75	" "
MgCO <sub>3</sub> . . . . .	54.70	" "
KCl . . . . .	2.80	" "
NaHCO <sub>3</sub> . . . . .	9.35	" "
	499.00	

**Note on the Colorimetric Methods for the Determination of Nitrates in Potable Waters.**—A. E. Johnson, Chem. News 61, 15.

The writer has used the "phenol-sulphuric acid method" with great success, but his solutions are made up differently from Dr. Rideal's (Chem. News 60, 261, this Journal 4, 67). 0.7215 gms. KNO<sub>3</sub> are dissolved in a liter of distilled water, and 100 cc. of this solution is then diluted to a liter with distilled water. 10 cc. of this solution is equivalent to 1 part of nitrogen as nitrates in 100,000. As regards the phenol sulphuric acid solution, HCl is used, which is necessary for a delicate reaction. Two parts by

measure of pure crystallized phenol, liquefied by heat, are poured into five parts by measure of pure concentrated  $\text{H}_2\text{SO}_4$ , and the whole is then thoroughly digested in a water-bath, kept boiling, for eight hours. When the mixture is cool,  $1\frac{1}{2}$  volumes of distilled water and  $\frac{1}{2}$  volume strong  $\text{HCl}$  for each volume of the above is then added. 80 cc. phenol, 200 cc.  $\text{H}_2\text{SO}_4$ , 420 cc.  $\text{H}_2\text{O}$ , and 140 cc.  $\text{HCl}$ , producing 840 cc. of a light brown solution, are mentioned as convenient quantities to take, and the water residue does not require treatment with water and sulphuric acid separately, but with this solution alone.

For analysis, 10 cc. of the water to be examined and 10 cc. of the standard potassium nitrate are pipetted into two small beakers, heated near the edge of an iron plate till nearly evaporated, when they are placed on a water bath and evaporated to complete dryness. 1 cc. of the phenol sulphuric acid is then added to each beaker, which are then placed on the water bath. When large quantities of nitrates are present, the liquid will speedily assume a red color. After standing fifteen minutes, the contents of the beakers are washed successively into a 100 cc. graduate, a slight excess (20 cc. say of 0.96 ammonia) added, and the solution is diluted to the mark with distilled water and transferred to a Nessler glass ( $6 \times 1\frac{1}{2}$  inches). The more strongly colored liquid is then transferred to the graduate again and the tints compared a second time, and thus the tints are adjusted.

In the case of very good waters, 20, 50 or more cc. should be evaporated to small bulk, rinsed into a small beaker, and treated as above, only 5 cc. of the standard potassium nitrate being taken ( $= 0.5 \text{ N in } 100,000$ ). Where the water is very bad, 10 cc. should be pipetted into a 100 cc. measuring flask, diluted to the mark with distilled water, when 10 cc. ( $= 1 \text{ cc. original water}$ ) are withdrawn and treated.

A. H. W.

**Coloration Determination of Nitric Acid, by Means of a Sulphuric Acid Solution of Diphenylamine.**—J. A. Müller, Chem. News 61, 100 (Bulletin de la Société Chimique de Paris).

5 cc. of the sulphuric solution of diphenylamine (0.2 gm. diphenylamine per liter of concentrated  $\text{H}_2\text{SO}_4$ ) are put into a clean test-tube of 15 centimetres, with 1 cc. of the solution of the nitrate to be examined. The tube is shaken, when a light blue tint

should appear. If not, the solution of nitrate is diluted until this result is obtained. With a little experience, solutions may be easily obtained containing from 0.5 to 5 mg. of nitric anhydride per liter. Standard solutions of potassium nitrate, containing 0.5, 1, etc., up to 5 mg. of  $N_2O_5$  in the form of nitrate to the liter, may be easily made up and kept for comparison. The method may be used for the determination of small quantities of nitric acid in arable soils or in drainage water, but the solution to be operated upon must be perfectly clear.

A. H. W.

## INORGANIC ANALYSIS.

**The Volumetric Determination of Copper.**—A. Etard and P. Lebeau, *Chem. News* **61**, 137 (*Comptes Rendus* **110**, 408).

The bromo-cupric coloration is used as an indicator. Any salt of copper, in a concentrated solution, when treated with an excess of concentrated hydrobromic acid, takes a violet color resembling permanganate. By using a standard solution of stannous bromide or chloride dissolved in strong hydrobromic acid, the decolorizing of the copper solution may be accurately employed as a method of determining the amount of copper.

A. H. W.

### **A New Method for the Analysis of Zinc and Copper Alloys.**

—H. N. Warren, *Chem. News* **61**, 136. Magnesium is the reagent used. In the case given for illustration, a brass alloy, the method is described as follows: A suitable weighed amount of the filings are dissolved in a small conical flask in strong  $H_2SO_4$ , when the solution is diluted with water to a convenient bulk. A few coils of magnesium wire are introduced, and the temperature of the solution is kept at about  $100^\circ F.$  until all the copper is precipitated, which is determined by testing the filtrate with potassium sulphocyanide. The copper is filtered, washed into a weighed platinum dish with a little ether, and the weight determined in the usual way. If other metals of the same group are suspected, the copper must be examined. To the filtrate, sodium acetate is added, and any iron present is precipitated as tribasic acetate, while the zinc is precipitated on a thick sheet or rod of magnesium, and is afterward treated as in the case of the copper.

A. H. W.

**The Determination of Nitrogen in Nitrates.**—Bailhache, Bull. soc. Chim., 3d series, 2, 9. This method is a modification of and an improvement upon that of Pelouze. Ferrous sulphate is used instead of the chloride.

The apparatus consists simply of a 250 cc. measuring flask supplied with a rubber cork pierced by a stop-cock funnel tube and a small tube drawn out at the upper end for the egress of gases.

The solutions required are as follows :

Standard ferrous sulphate solution, containing 100 grams of the crystallized salt and 75 cc of concentrated sulphuric acid per liter;

Standard bichromate of potash solution, 17.85 grams per liter ;

Standard solution of sodium nitrate, 50 grams per liter ;

A saturated solution of sodium bicarbonate ;

Dilute solution of potassium ferrocyanide.

The method is operated as follows :

50 cc of the ferrous sulphate solution and 25 cc. of concentrated sulphuric acid are introduced into the flask ; the sides of the flask are washed down by means of a pipette and it is then placed in a sand bath previously heated. The stop-cock being closed 25 cc. of the bicarbonate of soda solution is poured into the funnel and the stop-cock slightly opened so as to allow the liquid to run into the flask, drop by drop. It is essential to have it run very slowly. The solution soon begins to boil and remains in ebullition while the funnel is being emptied. Before it is quite empty, 10 cc. of the nitrate of soda solution is poured into it, or, in the examination of a commercial nitrate, 10 cc. of a solution obtained by dissolving 5 grams of the nitrate in 100 cc. of distilled water and filtering. The resulting disengagement of nitrogen dioxide is now watched carefully and not allowed to become rapid. When the nitrate solution is nearly all run out the stop-cock is closed and 25 cc. of the bicarbonate of soda solution again added. The stop-cock is opened slightly and the carbon dioxide is seen to expel the nitrogen dioxide from the solution, as is shown by the disappearance of the brown color. Just before the funnel is entirely empty the stop-cock is again closed and the solution allowed to boil for five minutes. The flask is then taken from the sand bath. The sides of the flask and the funnel tube are washed down and

the solution diluted to the mark with boiling distilled water. It is then cooled and again diluted to the mark. 200 cc. of the solution are now taken out and the unoxidized iron titrated by the bichromate of potash solution. From this the amount of nitrogen in the nitrate is easily calculated.

This method has been in successful operation for over two years in the agricultural laboratory of Seine-et-Oise. It is accurate and rapid, five determinations can be made in an hour. The method has been used successfully in the estimation of nitric nitrogen in food products.

The following table gives some results obtained in the above named laboratory :

Per cent of Nitrogen.	Schloesing- Grandeau Method.	Houzeau Method.	Ferrous Sulphate Method.	Theoretical Amount.
Pure sodium nitrate . . . .	16.45	. .	16.45	16.47
Nitrated superphosphate . .	5.45	5.40	5.50	. .
Commercial sodium nitrate {	15.80	. .	15.75	. .
	15.40	. .	15.45	. .
	15.65	. .	15.60	. .

I. A. P.

**Volumetric Determination of Zinc and Copper.**—E. Donath and G. Hattensaur, Chem. Zeit. 14, 323.

3-4 gms. of the zinc ore are dissolved in hydrochloric with the addition of a little nitric acid, and the solution diluted to a known bulk with water. A portion of this solution is filtered off, or drawn off by means of a pipette, and 25 cc. of concentrated tartaric acid solution are added. The mixture is made slightly alkaline with ammonia and heated to 80°. A standard solution of potassium ferrocyanide is run in from a burette until a drop of the solution gives a blue color by treating it with a drop of acetic acid on a porcelain plate. The iron is not precipitated in the presence of tartaric acid, but the latter does not affect the precipitation of the zinc. The end reaction is sharper with only a slight excess of ammonia. The potassium ferrocyanide solution is made by dissolving 33.5 gms. of the salt in one liter of water. 1 cc. of this solution corresponds to 0.010 gm. zinc. Some test analyses should be made first to become accustomed to the end reaction.

This same method may be used for the determination of copper

and thus avoid the removal of iron which is necessary in the cyanide method. It is necessary in this case to standardize the potassium ferrocyanide solution by a solution of pure copper, copper, containing 10 per cent. by volume of ferric chloride solution (1:10). The solution of copper for analysis must contain no excess of ammonia and must be as near the neutral point as possible. The end reaction is determined by bringing a drop of the solution with some of the precipitate on a piece of thick filter paper and placing a drop of acetic or dilute hydrochloric acid (1:3) on the same spot. An excess of ferrocyanide solution is denoted by a blue color, or precipitate that will not mix with the copper precipitate. In case both metals are present in an ore, they are determined together by titrating with ferrocyanide solution. Another portion of the solution is shaken with iron filings to separate the copper, and the filtrate from this is oxidized with nitric acid, and the zinc determined in the manner prescribed. The difference in the two results will give the amount of copper. A mixture of the two metals which gave, gravimetrically, 65.07 per cent. Cu and 35.09 per cent. Zn, gave, by the method just described, 65.01 per cent. Cu and 35.02 per cent. Zn. S. C.

**Estimation of Cadmium in Zinc Refuse.**—W. Minor, Chem. Zeit. 14, 4.

The method already described\* in which a weighed quantity of the substance is dissolved in hydrochloric acid and the cadmium is separated from zinc and iron by sulphuretted hydrogen has been shortened by the author. The precipitate, which always contains a little zinc, is washed with hot water and dissolved in dilute hydrochloric acid. This solution is then heated to boiling and the cadmium is precipitated by a hot solution of sodium hydroxide. The precipitated cadmium hydroxide is filtered off and washed with a 1 per cent. caustic soda solution to remove traces of zinc, and finally with hot water, to remove the alkali. To prevent loss by reduction, the filter is ignited in a current of oxygen and weighed. If iron is not present, the precipitation with sulphuretted hydrogen may be omitted and the cadmium at once precipitated by caustic soda. To estimate zinc and cadmium in zinc blends the following method is used†: The ore is dissolved

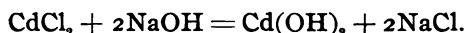
\*This Journal 4, 80.

†Chem. Zeit. 14, 34.

in the usual manner, and the iron is precipitated by an excess of ammonia which keeps the zinc and cadmium in solution. The filtrate is nearly neutralized with hydrochloric acid, and a hot solution of caustic soda is added, which precipitates the cadmium and keeps the zinc in solution. The cadmium is weighed as described above, and the zinc solution is nearly neutralized with hydrochloric acid and titrated with a standard solution of sodium sulphide.

Besides the methods just given, the author describes two by volumetric analysis.\* The first, or indirect method, he recommends for rapidity. The weighed sample is dissolved in hydrochloric acid and the insoluble residue filtered off.

The cadmium is precipitated from this solution by sulphuretted hydrogen and the precipitate is carefully washed and weighed. The amount of arsenic that may be present is usually too small to be taken into account. The precipitate is then redissolved in dilute hydrochloric acid and treated with an excess of caustic soda solution, which reprecipitates the cadmium. The zinc in the filtrate is determined by titrating the solution with standard sodium sulphide and the amount of zinc sulphide found, subtracted from the weight of the impure cadmium sulphide, will give the weight of the cadmium as sulphide. In the direct method the cadmium is titrated, in a neutral solution, with standard sodium hydroxide.



It is necessary in this method to remove all metals that are acted upon by sodium hydroxide. The cadmium is separated from the iron and zinc by the methods already described and the pure hydroxide thus obtained is dissolved in dilute hydrochloric acid and the solution evaporated to dryness. The residue is taken up with water and a very slight excess of acid, and again evaporated to dryness; after which it is taken up with water and titrated with normal soda solution. The end reaction is best obtained by putting a drop of the solution on sodium sulphide or red litmus paper.

S. C.

**Determination of the Oxides of Iron and Aluminum in Phosphates.**—R. Jones, *Chem. Zeit.* 14, 269.

The author recommends Glaser's method in which 5 gms. of

\**Ibid.*, 348.

the phosphate is dissolved in aqua regia and diluted to 500 cc. 100 cc. of this solution is shaken with 25 cc. sulphuric acid (sp. gr. 1.84) for five minutes and after cooling, 100 cc. of 95% alcohol are added, and the solution is shaken again. Alcohol is again added to supply the loss in bulk by contraction and after standing half an hour the solution is filtered and 100 cc. of it (= 0.4 gm. phosphate) is placed in a platinum dish and heated until the alcohol is all driven off. The solution is then washed into a beaker with 50 cc. water and heated. Ammonia is cautiously added until the solution is alkaline, after which it is heated until the excess of ammonia is driven off. The precipitate is then filtered off, dried and weighed and half the weight is taken as the oxides of iron and aluminum. The calcium may be determined from the sulphate which separates after the addition of the alcohol. Magnesia may be determined in the filtrate from the iron precipitate. Stutzer\* separates the iron and aluminum by making the hydrochloric acid solution alkaline with ammonia and then slightly acidifying with acetic acid. The precipitated iron and aluminum phosphate is filtered off, washed, and then titrated in a beaker with 150 cc. of molybdate solution in the usual manner to separate the phosphoric acid. The filtrate from the yellow precipitate is heated for 10 minutes on a water bath and the iron and aluminum is precipitated by ammonia. This precipitate is purified by dissolving in hydrochloric acid and reprecipitating with ammonia.

The author claims that the accuracy of this method varies according to the amount of calcium acetate and acetic acid present, and recommends a combination of these methods for accurate results.

S. C.

**The Estimation of Iron-oxide in Phosphate.**—A. Stutzer, *Ztschr. angew. Chem.* 1890, 43.

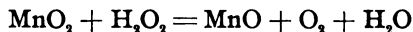
The method consists in precipitating the iron, alumina and phosphoric acid in an ammonium acetate solution, filtering and treating the precipitate with molybdate solution, when the phosphoric acid is precipitated. This is filtered, and the iron and alumina precipitated from the filtrate by ammonia. J. E. W.

\**Ztschr. f. angew. Chem.*, 1890, 43.



**The Analysis of Pyrolusite by Means of Hydrogen Peroxide.**—A. Baumann, *Ztschr. angew. Chem.* 1890, 72.

When a strongly acidified solution of hydrogen peroxide is poured into finely ground pyrolusite, or when a neutral solution is added to a mineral acid in which is suspended pulverized pyrolusite, the action that takes place is expressed thus :



i. e., 86.72 parts of  $\text{MnO}_2$  gives off, with an excess of acidified hydrogen peroxide, 31.92 parts of oxygen, while the excess of the peroxide remains unchanged. To put to use this reaction, the author uses an apparatus very similar to that of Fresenius and Will. In one flask is placed the weighed sample with 30 cc. of 1-3 sulphuric acid. An excess of hydrogen peroxide is put into the connected flask and the apparatus weighed. The peroxide is then gently forced over into the mineral, and the action begins at once, continuing until all the pyrolusite is decomposed. Air is then drawn through the apparatus to replace the oxygen and have the conditions the same as when the first weight was taken. The apparatus is then weighed, the loss in weight being the oxygen evolved.

The author also uses the peroxide in the titration method. The weighed sample of pyrolusite is placed in a flask or tall beaker and the acid solution of peroxide is allowed to flow on it. When all action has ceased, the remaining peroxide is titrated with standard permanganate solution.

The paper concludes with the application of hydrogen peroxide in determining the volume of gas given off when pyrolusite is treated with it.

J. E. W.

**Estimation of Free Hydrochloric Acid in Solution of Stannous Chloride.**—W. Minor, *Ztschr. angew. Chem.* 1890, 25. In estimating the hydrochloric acid in solutions of stannous chloride, the method with silver nitrate is not applicable, in consequence of the separation of the combined tin. Therefore, it is better to proceed in the following manner: Dilute 10 cc. of the solution to be examined with water, and add to the hot liquid sulphuric acid until no more precipitate appears. Filter into a liter flask and fill the flask to the mark. Boil 500 cc. of the well

shaken filtrate, which is equal to 5 cc. of the original solution, to drive off any hydric sulphide and determine the hydrochloric acid with standard soda solution.

From the amount of tin calculate the amount of combined chlorine and subtract this from the total amount obtained by the titration.

J. E. W.

**Estimation of Carbonic Acid in Drinking Water Containing Magnesia.**—H. Trillich, *Ztschr. angew. Chem.* 1889, 337.

100 cc. of the water is mixed in a stoppered settling cylinder, with 5 cc. barium chloride solution (1:10) and 45 cc. of titrated baryta water (7 gms. of the hydroxide and 0.2 gm. of the chloride per liter) and allowed to settle for 12 hours after being well shaken.

Two portions of 50 cc. each are removed and titrated with hydrochloric acid, of a strength that 1 cc. = 1 mg.  $\text{CO}_2$ , using phenolphthalein.

Determine the  $\text{MgO}$  gravimetrically.

If (a) = the number of cc. of acid necessary for 45 cc. of the baryta, (b) = the number of cc. of acid used by the 50 cc. of the clear solution, and (m) = the milligrams of  $\text{MgO}$  in 100 cc. of the water to be tested, then  $(a - 3 \times 6 - 1.1 \times m) 10 =$  the number of milligrams of free and loosely combined  $\text{CO}_2$  in a liter.

For the total  $\text{CO}_2$  use the remaining 50 cc. in the settling cylinder, titrating with the same acid, using cochineal tincture.

If (d) = the number of cc. of acid and  $(d - b - 1.1 \times m) 10 =$  the milligrams of total  $\text{CO}_2$  in a liter.

**Note on Pretended Reagent for Copper.**—A. and P. Buissine, *Bull. soc. Chim.*, 50, 517.

The authors find that the new reagent for copper announced by Aliamet (*Bull. soc. Chim.*, 47, 754.)\* gives the same reaction, a rose coloration, with solutions of other metallic salts, and even with distilled water. The reagent consists of a saturated aqueous solution of neutral sodium sulphite to which is added a small quantity of pyrogalllic acid. It is shown that the rose solution produced when this is added to a solution is due to the presence of free oxygen in the liquid. If it is added to boiled distilled water, no coloration is observed, but on vigorously stirring the water,

\*This Journal 1, 414.

the rose tint makes its appearance. The same effect is seen in solutions of metallic salts. Neutral sodium sulphite being alkaline, the reagent is nothing more than an alkaline solution of pyrogalllic acid, a solution which is sometimes employed in laboratories for absorbing oxygen.

I. A. P.

**The Volumetric Determination of Acids.**—G. Linossier and M. Lignon, Bull. soc. Chim. **50**, 46, 353, 354.

The method can be applied to all acids capable of forming with one of the metals precipitated by hydrogen sulphide in acid solution an insoluble combination. The acid is separated by adding a solution of one of these metals and decomposing the precipitate thus formed with hydrogen sulphide. The free acid is then titrated with standard caustic soda, using methyl orange as indicator.

Sulphuric, phosphoric and hydrochloric acids are determined as follows :

*Sulphuric acid.*—The solution of sulphate, not containing more than .1 gram of sulphuric acid, is placed in a capsule, one or two volumes of alcohol added, the solution heated nearly to boiling, and the sulphuric acid precipitated by a slight excess of neutral lead acetate. The lead sulphate settles rapidly and upon cooling, the clear liquid is poured upon a filter and the precipitate in the capsule washed by decantation with a mixture of alcohol and water, care being taken to throw as little as possible of the precipitate upon the filter. When the washing is completed the funnel is placed over a flask and a saturated solution of hydrogen sulphide poured upon the filter, to convert the traces of lead sulphate into sulphide. The same solution is then poured upon the mass of lead sulphate in the capsule and the mixture well stirred. After a few moments, the whole is thrown upon the filter and the precipitate washed with water containing hydrogen sulphide. The free acid in the filtrate is then titrated with normal caustic soda solution, using methyl orange as indicator. Results are accurate. Other acids precipitated by lead salts, must of course be absent, as well as free nitric acid, ammoniacal salts, etc., which produce turbidity in the solution.

*Phosphoric acid.*—The phosphate solution, free from hydrochloric or sulphuric acid is acidified with nitric acid, excess of bismuth nitrate added and the liquid heated nearly to boiling. The

phosphoric acid is completely precipitated as bismuth phosphate. This is then subjected to precisely the same treatment as that prescribed for the lead sulphate in the preceding note, except that hot water is used for washing, instead of dilute alcohol. The free acid is separated and estimated as above. Results exact.

*Hydrochloric acid.*—The cold, or slightly warm solution is treated with a feeble excess of mercurous nitrate, by which the chlorine is thrown down as mercurous chloride. Subsequent treatment the same as in the case of the other two acids.

This method can be used to advantage in the determination of chlorine in urine.

I. A. P.

**The Separation and Estimation of Zinc.**—J. Ribon, Bull. soc. Chim. 50, 518.

By this method the zinc is converted into soluble hyposulphate (dithionate,  $\text{ZnS}_2\text{O}_6$ ) by the addition of sodium or barium hyposulphate, and then precipitated in the cold with sulphuretted hydrogen. The precipitate thus obtained settles rapidly, is dense, and can be washed by decantation. The separation of the precipitate from the solution is complete, and the hyposulphuric acid set free has but little solvent action upon it in dilute solutions.

The method is operated as follows: The solution containing the zinc is treated with sodium carbonate until the appearance of a slight permanent precipitate, which is redissolved with a few drops of hydrochloric acid. To the solution, slightly acid, an excess of sodium or barium hyposulphate, preferably the sodium salt, is added, more than sufficient to effect the double decomposition. A large excess produces no evil results.

The liquid is then diluted so as to contain not more than .1 gm. zinc per 100 cc., and a current of sulphuretted hydrogen passed through the cold solution. A heavy white precipitate is thrown down immediately, the supernatant liquid becoming clear as soon as the zinc is all converted into sulphide. After allowing to stand a few moments, the precipitate is washed by decantation several times with boiling water containing sulphuretted hydrogen, and then thrown on the filter, where the operation is completed with a few more washings. The sulphide is dried at  $100^\circ$  and the filter paper incinerated in a crucible with a small amount of ammonium

nitrate. It can then be ignited with sulphur in a current of hydrogen or converted into oxide by calcination.

The following results show the accuracy of the method, as well as the necessity of precipitating in a dilute solution.

Zinc contained in the solution.	Volume of the solution.	Zinc found.	Difference.
0.2299	90	0.2279	0.0020
0.2378	90	0.2357	0.0021
0.2206	128	0.2196	0.0010
0.2321	136	0.2316	0.0005
0.2415	236	0.2413	0.0002
0.2309	240	0.2308	0.0001
0.2404	243	0.2404	0.0000
0.2548	270	0.2543	0.0005

By this method zinc can be separated from the alkalies and alkaline earths. For the estimation of the former it is necessary, of course, to use barium hyposulphate.

Iron and manganese are not precipitated by sulphuretted hydrogen in presence of hyposulphates, and hence zinc can be estimated in presence of these metals.

I. A. P.

**A New Method for the Analysis of Pyrites.**—P. Jannasch, *Chem. News* 61, 114 (*Journ. für prak. Chemie*).

Air passes from a gas holder, first, through concentrated sulphuric acid, next through a Drechsel flask containing 50 cc. of fuming nitric acid, then through a tube of potash-glass, laid in a combustion furnace, and containing the boat filled with the finely pulverized pyrites. Attached to the combustion tubing is a tubulated receiver charged with 100 cc. bromine water, then a Peligot tube, containing 40 cc. bromine water is next attached, and finally a cylinder of distilled water. To commence the decomposition, a current of air (150 to 200 bubbles per minute) is passed through the apparatus, and the substance is then heated, beginning at the back. The front end of the tube is heated to drive the sulphuric acid into the absorption vessels as fast as formed. The reaction is allowed to proceed for about three-quarters of an hour, when the tube is cooled in a slow current of air, after removing the flask containing the nitric acid. The tube is finally strongly ignited, but not at so high a temperature as to soften the glass tube. After complete decomposition, the contents of the receivers are rinsed

into a beaker, excess of bromine is evaporated off, 1 cc. of strong hydrochloric acid is added to the solution, and the sulphuric acid is precipitated by a sufficient amount of barium chloride. Before washing on the filter, the precipitate is purified by decantation with boiling water containing hydrochloric acid, in order to remove any barium nitrate which may have been carried down. It is recommended to treat the ignited barium sulphate with dilute hydrochloric acid, and reweigh. The ferric oxide remaining in the boat is, with the latter, placed in a flat porcelain or platinum capsule, and the oxide is dissolved in strong hydrochloric acid on the water-bath. The iron solution is then evaporated almost to dryness and silica is separated.

A. H. W.

**On the Decomposition of Sulphides (Bournonite, Proustite, etc.) in a Current of Air Charged with Bromine.**—P. Jannasch, *Chem News*, 61, 114, (*Jour. für prak. Chemie*).

Air is passed, from a gas-holder, through a Drechsel drying cylinder charged with concentrated sulphuric acid, then through another cylinder containing 50 cc. of bromine, then through a tube of potash-glass 20 cm. in length, in which the boat with the substance is heated, finally entering receivers filled with a mixture of equal volumes of dilute hydrochloric acid (1:4) and a ten per cent. solution of tartaric acid. The author was not successful in decomposing the sulphur bromide formed by treatment with chlorine water or potassium chlorate, but by adding to the liquid from the receiver an excess of bromine, and heating on the water-bath, constantly stirring, the sulphur bromide was all dissolved, and the sulphuric acid was then precipitated by barium chloride. The antimony and arsenic are next separated in the usual manner from the filtrate. The portion containing the non-volatile bromides, lead, copper, silver, etc., is heated with nitric acid in a beaker on the water-bath for about an hour, when the lead, copper, etc., are dissolved. In order to effect this readily, the heat applied to the substance in the boat is never allowed to reach such a degree as to fuse the bromides formed. When silver bromide is simultaneously present, the material is carefully crushed in the liquid with a glass rod, the insoluble matter (silver bromide, gangue, etc.) is filtered off, the acid solution is evaporated to dryness, and lead, copper and nickel are separated as usual. The silver

bromide and gangue are then digested with a dilute solution of potassium cyanide (2-4 gms. of a pure preparation), when the bromide is dissolved and collected by filtration. The filtrate is precipitated by nitric acid in a porcelain capsule, the solution is dried with the precipitate to destroy small quantities of silver cyanide, if formed, the residue is reheated with water, nitric acid and bromine water, and filtered off and weighed. The bromine used must be first tested for the possible presence of sulphuric acid. If argentiferous sulphides are under examination, the absence of chlorine from the bromide must be assured, and to do this the reagent is first shaken up with powdered potassium bromide, allowed to stand, then filtered through slag-wool. Decided advantages recommend the substitution of bromine for chlorine in the determination of sulphides, and accurate results are given by the above method.

A. H. W.

**On the Decomposition of Pyrites in a Current of Oxygen.**

—P. Jannasch, *Chem. News* **61**, 124 (*Jour. für prak. Chemie*).

The author simplifies his process for the decomposition of pyrites by substituting oxygen for air and nitric acid (*Chem. News* **61**, 114). The apparatus is the same as that described in the previous paper, except the gas-holder is filled with oxygen and the nitric acid bottle is omitted. Care must be exercised in heating the tube, to avoid any spirting of the substance or sublimation of sulphur. About 200 bubbles of oxygen per minute are forced through the apparatus. After half an hour the tube is strongly ignited for a quarter of an hour longer, and the boat is drawn out after the tube has cooled a little, and the oxygen current is shut off. The sulphuric acid is precipitated in the receivers by barium chloride. A determination of sulphur in pyrite may be made by this method, it is stated, in from four to six hours.

A. H. W.

**Separation of Vanadic and Tungstic Acids.**—C. Fredheim (*Ber.* **23**, 353).

The concentrated solution of the salts is treated, in a large porcelain evaporating dish upon the water-bath, with a concentrated solution of mercurous nitrate as nearly neutral as possible until the precipitate settles well, and then an excess of freshly

precipitated mercuric oxide added to neutralize the solution, and the whole digested for twenty minutes. After cooling, the precipitate, consisting of a mixture of the mercury salts of both acids with an excess of mercuric oxide is filtered off and washed with water to which a few drops of mercurous nitrate have been added. The precipitate is then, with the aid of a jet of water from the wash bottle, washed into the dish in which the precipitation was made and evaporated to the consistence of paste. After cooling, the mass is treated with very strong hydrochloric acid, covered with a watch glass, and heated over the water-bath for five minutes.

By this means all the vanadium dissolves as vanadyl chloride, and almost all the tungsten and mercury dissolve, since the chlorine formed converts nearly all the mercurous into mercuric chloride. The precipitate remaining on the filter is dissolved in hydrochloric acid, sp. gr. 1.12, and added to the main solution. To the blue solution a considerable amount of water is now added when almost all of the tungstic acid precipitates, vanadium and mercury remaining in solution. After standing twenty-four hours to allow all the tungstic acid to separate.

E. H.

**The Detection and Determination of Chlorine in Sulphocyanide of Potassa.**—C. Mann, *Zeitschr. anal. Chem.* **28**, 668.

If an alkaline sulphocyanide is mixed with a solution of sulphate of copper, and sulphuretted hydrogen passed through the solution, there will appear at first a precipitate of sulphocyanide of copper, and only after a longer passage of the gas will sulphide of copper be formed. If there is more copper in the solution than is necessary for the formation of sulphocyanide of copper, and if the passage of the sulphuretted hydrogen is stopped, the moment the liquid becomes brown or when all the sulphocyanide of copper is precipitated and the sulphide of copper begins to form, but does not appear agglomerated, and if a sufficient amount of sulphate of copper is added to fix the free sulphuretted hydrogen and to precipitate again any sulphocyanide acid that may have become free, the filtrate will give no reaction for sulphocyanide. If the sulphocyanide contained even a very small amount of chlorine or bromine it may be readily detected by adding a little nitric acid and a few drops of nitrate of silver. The author advises that 5 gms.

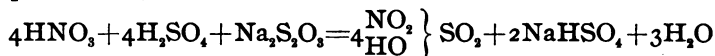


of the sulphocyanide be taken and 20 gms. pure sulphate of copper, each salt dissolved in 100 cc. water and the two solutions poured together. After passing sulphuretted hydrogen as directed above, 8 gms. of sulphate of copper in 40 cc. of water are added, and the whole stirred briskly and filtered. The test analyses, when weighed quantities of pure chloride of ammonium were added, were very satisfactory.

A. A. B.

**Determination of Nitrogen in Nitric Acid by Kjeldahl's Method.**—Dr. Otto Foerster, *Zeitschr. anal. Chem.* **28**, 422.

The author finds that the use of phenol-sulphuric acid in the determination of nitrogen in nitric acid salts by Kjeldahl's method gives results slightly low, because a small amount of nitric acid is volatilized before it had time to act on the phenol. This loss may be avoided by adding after the phenol-sulphuric acid a substance capable of changing the nitric acid into a form volatile only at a high temperature. After many experiments the author found that hyposulphite of soda answered the purpose admirably. This salt, as is well known, gives as a final result of reaction with sulphuric and nitric acid, the so-called lead chamber crystals, nitrosyl sulphuric acid,



Besides this, the hyposulphite influences beneficially the transmission of all the products of decomposition of nitric acid into the stable combination which gives up its nitrogen easily to phenol by heating. The phenol-sulphonic acid should contain about 5 to 6 per cent. phenol, as more than 7 per cent. or less than 3 per cent. phenol gave results decidedly too low. The hyposulphite should be used in coarse powder. For the absorption of the ammonia formed the author uses a one-fifth normal sulphuric acid and titrates it with a one-fifth normal caustic soda. As an indicator, he uses a solution of 9 gms. litmus, purified by Bosetti's method, and 1 gm. malachite green in a liter of alcohol, of which 8 to 10 drops is sufficient to give the proper color to the acid to be titrated. The malachite green causes the litmus which is violet in a neutral solution to change more sharply to blue. The method of procedure is as follows: Weigh off so much of the solution containing nitrate of potassa or soda as will give a con-

venient amount of the salt, say  $\frac{1}{2}$  to 1 gm.; place it in the flask in which the operation is to be conducted, and evaporate it to dryness. Add phenol-sulphonic acid in about the proportion of 30 cc. of the acid to 1 gm. of the dry salt, and when the dry mass is perfectly dissolved in the cold, add 1 to 2 gms. of hyposulphite of soda. When this has dissolved, add sulphuric acid in the proportion of 10 cc. sulphuric acid to 15 cc. phenol-sulphonic acid and 0.4 to 0.5 gm. metallic mercury. Close the flask instantly and heat it, proceeding exactly as in Kjeldahl's method. To avoid the loss of time incident to weighing the mercury the author uses a glass tube of the form shown in the cut. The tube is fused together at one end and cut half way through with a file, so that the little cup thus formed will hold the required amount of mercury. By dipping the tube in the mercury and tapping it sharply after withdrawing it, the excess of mercury is shaken out, and then by placing the finger over the file cut and reversing the tube, the mercury is poured into the flask through the open end of the tube. The oxidation of the organic bodies and the transformation of the nitrogen to ammonia requires from 1 to  $1\frac{1}{2}$  hours. Sometimes a reddish substance is formed, which resists oxidation for a long time; the appearance of this substance, however, has no influence on the result of the analysis. The author found a constant loss when using the ordinary form of apparatus, so that he finally adopted the apparatus described in Fresenius' Quantitative Analysis, 6th (German) Ed. I, 224, using as an absorption tube one in which the ammonia charged air was obliged to pass through several bulbs containing the one-fifth normal sulphuric acid. The results obtained with these final precautions on  $\frac{1}{2}$  gm. nitrate of potash were most satisfactory. A. A. B.

## IRON AND STEEL.

EDITED BY P. W. SHIMER.

**On the Determination of Minute Quantities of Aluminum in Iron and Steel.**—John E. Stead, F. I. C., J. Soc. Chem. Ind., 1889, 965. For the determination of aluminum the following reagents are required:

- (1.) Pure hydrochloric acid.
- (2.) Ammonia.

- (3.) Pure sodium hyposulphite (sat. sol.)
- (4.) Sodium or ammonium phosphate (sat. sol.)
- (5.) Sodium hydrate, free from alumina and silica. That prepared from sodium is best.
- (6.) Washed filter paper of C. Schleicher and Schüll.  $4\frac{1}{2}$  or 5 inches.

The method, as described by the author, is as follows: Weigh out 11 or 22 gms. of the iron or steel to be examined; the smaller quantity preferable unless less than 0.01 per cent. of aluminum is expected. Dissolve the 11 gms. in 44 cc. HCl or the 22 gms. in 88 cc. on the sand bath in a 600 cc. beaker. When dissolved, evaporate to dryness and redissolve residue in HCl and hot water; filter off from silica, collecting the filtrate in a 500 cc. beaker, and wash the silica clean. Let the total bulk of the filtrate and washings not exceed 200 cc.

To separate the alumina from the main bulk of the iron, add 3 cc. phosphate solution, then dilute ammonia till the free acid is neutralized—this point is readily known by a small quantity of phosphate of iron and alumina remaining insoluble after repeatedly shaking the solution. Add HCl drop by drop till the solution is clear, and then set the beaker on the bath to boil. As soon as the boiling commences, add a large excess of the sodium hyposulphite solution (50 cc. is sufficient), and continue boiling till the solution does not give off  $\text{SO}_2$ . If there is doubt whether or not there is excess of hyposulphite, add a few more cc., and if this does not give a precipitate of sulphur, sufficient hyposulphite has been added.

One hour's boiling will eliminate all the  $\text{SO}_2$ . The precipitate must now be collected on a 5 inch washed filter-paper, and be well washed with boiling water to free it from all soluble iron and other salts.

Dissolve all soluble matters out of the precipitate by pouring over it 5 cc. HCl and 5 cc. boiling water, allowing the solution to flow into the beaker in which the alumina was originally precipitated. Wash out of the filter all soluble matters with a small nozzle in the wash bottle. Only sulphur will be left on the filter.

The solution must now be transferred to a platinum dish, and evaporated to dryness over a beaker of boiling water. When dry,

add 2 gms. pure sodium hydrate, placing it on the bottom of the dish, and then add about 1 cc. of boiling water to partially dissolve the hydrate. Place the dish over the flame of a Fletcher's rose burner till the mass is in a state of tranquil fusion. Allow to cool, and add 50 cc. boiling water, and place the dish and contents over a Bunsen burner, and boil five minutes. More water must be added, so that the total bulk measures 110 cc. Filter off the insoluble oxides through a  $4\frac{1}{2}$  inch washed dry filter-paper. The first portions which pass through will be turbid, and must be refiltered.

When 100 cc. (= 10 gms. of steel) have passed through, measure that quantity off exactly, and reject the insoluble matter and the residue of the solution. Neutralize the NaHO with HCl till the solution reddens litmus paper, and add 3 cc. sodium phosphate, and then hyposulphite of soda in large excess. Boil till all  $\text{SO}_2$  is expelled, and add 2 cc. ammonium acetate, boil for two minutes longer, and filter through a  $4\frac{1}{2}$  inch washed filter, wash with boiling water till the washings are free from chlorides; burn off, wet or dry, and weigh. The precipitate is  $\text{AlPO}_4$ , and contains 22.36 per cent. aluminum. P. W. S.

**Analysis of Tungsten, Ferro-Tungsten, Tungsten Steel, Ferro-Chromium, and Chromium Steel.**—A. Ziegler, Dingl. Polyt. J. 274, 513-528. The J. Soc. Chem. Ind. 1890, 216-218, contains a useful abstract of this paper. P. W. S.

**Titanium in Blast-Furnaces.**—Auguste J. Rossi, J. Am. Chem. Soc. 1890, 91, 117. A large amount of information on the effect of titanium in the blast furnace is gathered together in this paper. The author submits the following conclusions:

1°. Titanic acid is not necessarily and always a cause of trouble in the blast furnace, even if present in large quantities.

2°. In small quantities its presence appears to have been ignored for many years, and furnaces have run, and do run to-day, with ores rich in iron, containing from .30 per cent. to 1 per cent. titanic acid in the charges, without apparent trouble of any kind, these ores being smelted alone or in admixture with others more or less free from titanium.

3°. When present in very notable quantities, it has a tendency

to render the slag pasty and clog a furnace with titanium deposits if it is not made, by a judicious treatment, to pass into the slag.

4°. With a judicious adaptation of the fluxes to the composition of the ores, with a view to obtaining a slag of a certain character and to the production of special grades of pig-metal adapted to the given circumstances, lean ores containing 40 to 48 per cent. of titanitic acid have been successfully smelted in a regular manner for years, but at a much greater expenditure of combustibles.

5°. The titaniferous ores appear to be "*par excellence*" Bessemer ores, containing little or no phosphorus, and they form, both in Europe and many states of the Union and Canada, enormous deposits now useless.

P. W. S.

**Scheme for Analysis of Metallic Aluminum.**—Alfred E. Hunt, John W. Langley and Charles M. Hall, Trans. Am. Inst. Min. Eng., Feb., 1890. The following are the methods used in the Pittsburgh Testing Laboratory for the analysis of aluminum:

*Determination of Iron.*—Dissolve from 1 to 5 gms. of the metal in hydrochloric acid, and reduce with stannous chloride, taking up the excess of stannous chloride with bichloride of mercury. Titrate with a standard solution of bichromate of potash.

*Silicon.*—Dissolve 1 gm. of the metal in aqua regia composed of equal parts of nitric and hydrochloric acids; evaporate to dryness; take into solution with 5 cc. strong HCl; add water, boil and filter off the gray residue; wash with dilute HCl; ignite and weigh as silicon, plus silica; fuse with carbonate of soda; dissolve in dilute HCl; evaporate to dryness; redissolve in dilute HCl, and filter off total silica. The difference between the weight of the silicon and the silica being the oxygen which is united with the graphitoidal silicon, from which the amount of graphitoidal silicon can be calculated.

*Copper and Lead.*—Dilute the filtrate from the silica till free HCl is only about 1 per cent. of the solution. Pass  $H_2S$  through the hot solution, and filter off sulphides of copper and lead. Dissolve in 1.2  $HNO_3$  and filter off sulphur. Add 5 cc.  $H_2SO_4$ , and evaporate to fumes of  $SO_3$ . Dilute, and, after waiting some time, filter from sulphate of lead into a platinum dish. The lead sulphate should be weighed, and lead calculated from it. Nearly

neutralize with ammonia, leaving about 2 drops  $\text{H}_2\text{SO}_4$  (dilute), and precipitate copper by battery.

*Aluminum*.—Receive filtrate from sulphides of copper and lead in 500 cc. flask, and dilute to 500 cc. mark with water. Take 50 cc. of the solution (equal to one-tenth gm. of the metal), boil off the free  $\text{H}_2\text{S}$ , oxidize the iron in solution with a little bromine water, and add sufficient ammonia to precipitate the sesquioxides of iron and alumina, which, after careful washing, ignite and weigh. Subtract the  $\text{Fe}_2\text{O}_3$  calculated from the iron found by titration, and the weight of any phosphoric acid which may be present, and calculate the remainder as  $\text{Al}_2\text{O}_3$ , from which the percentage of aluminum can be readily reckoned.

*Calcium*.—A trace may be found in the filtrates from iron and alumina, and is separated in the usual way. The filtrates from the calcium can be readily examined for magnesium.

*Alkalies*.—Dissolve 1 gm. in  $\text{HCl}$  and evaporate in a platinum dish to separate the silica, and proceed as usual until the sesquioxides of alumina and iron are precipitated with ammonia. Dissolve this, after washing, in nitric acid, in platinum, and evaporate to dryness on the water bath. Finally, heat over a small flame until the nitrate of alumina is all decomposed. This condition is indicated when the residue is white and friable, and no acid fumes can be detected by ammonia. Treat residue with hot water and get alkali nitrates in solution. This, together with the filtrate from alumina, contains all the alkali present, which should be evaporated, and after separating contained portions of lime and magnesia, weighed as chlorides.

P. W. S.

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## ORGANIC ANALYSIS.

**Method for the Determination of Quinine in Tannate of Quinine.**—Dr. Sigmund Neumann, *Ztschr. anal. Chem.* **28**, 663.

The method prescribed by the Hungarian pharmacopoeia for the estimation of quinine in tannate of quinine was found by the author to give utterly unreliable results. This method—Orrillard's—is essentially as follows: Evaporate to dryness the tannate of quinine mixed with recently slacked lime, and extract with hot alcohol. Acidulate the alcoholic solution with sulphurous acid,

evaporate to small volume, and after six hours filter. Precipitate the quinine in the filtrate by caustic potassa, filter on a weighed filter, wash slightly, dry at  $90^{\circ}$  and weigh. The author prepared tannate of quinine which contained by calculation 25–30 per cent. quinine, but obtained by the above method of analysis only from 7 to 13 per cent. After many experiments he worked out the following method: Weigh 2 gms. of tannate of quinine into a glass cylinder of 300 cc. capacity provided with a carefully ground-in glass stopper, into which has been previously placed 20 to 25 cc. of caustic potassa solution, sp. gr. 1.240, and shake well. Dilute to 60 or 80 cc., add exactly 100 cc. ether, close the cylinder quickly with the stopper, and shake well. After standing a few minutes two strata are formed, the colorless ether above and the caustic potassa solution colored brown by the tannic acid, below. No solid particles should be seen floating in either stratum, as their presence is indicative of impurities in the tannate of quinine or of imperfect solution. If the potash solution is too dark to be transparent, it must be diluted. When the two strata have separated completely, open the cylinder, draw up quickly into a pipette 50 cc. of the ether, transfer it to a weighed capsule, evaporate the ether at a gentle heat, dry at 100 degrees, and weigh the quinine. This weight gives the percentage of quinine directly. This residue may be examined for other alkaloïds. It should be completely soluble in dilute hydrochloric or sulphuric acid; if it is not, the ether is impure or the preparation contains fats, resins, etc. Results may be easily obtained by this method in  $1\frac{1}{2}$  hours, but they are slightly high, owing to the rapid evaporation of the ether and to its slight solubility in water. The author to discover the cause of the inaccuracy in Orrillard's method made a determination by it and found 13.1 per cent. quinine. He then dissolved the lime (which had been extracted with alcohol) in hydrochloric acid, precipitated by caustic potassa, agitated with ether, and found an additional 6.2 per cent. quinine. He then agitated the caustic potassa and wash water used to precipitate and wash the quinine in Orrillard's method with ether, and obtained from this 5.7 per cent. quinine. The amounts added together give 25 per cent. quinine, a result agreeing very closely with those obtained by his own method, This shows:

1. The alcohol does not extract all the quinine from the lime :
- and 2, That the quinine is soluble in the caustic potassa and wash water.

A. A. B.

**The Estimation of Benzene in Illuminating Gas.**—Berthelot, Bull. soc. chim. **50**, 660.

In this paper the author refers to his published method (Ann. chim. phys., 5th series, **10**, 171, and **12**, 289) for the estimation of benzene in illuminating gas by means of fuming nitric acid. 20 or 22 cc. of the gas is collected over water in a small flask and 1 cc. of fuming nitric acid introduced. The mixture is then shaken for a half minute and the nitro-benzene formed collected and weighed. If the action be continued longer, other constituents of the gas will be oxidized ; hence, great care is necessary in order to secure good results.

I. A. P.

**Contributions to the Examination of Milk.**—Isbert & Venator, Ztschr. angew. Chem. 1890, 85. Some results of the work done at the Saarbrück experimental station.

**Analysis of Baking Powder.**—C. A. Crampton, The Analyst **15**, 26 ; Bull. U. S. Dept. of Agriculture, No. 13. The powders are divided into three classes, viz.:

1. Tartaric powders, in which the acid constituent is tartaric acid in some form.
2. Phosphate powders, in which the acid constituent is phosphoric acid.
3. Alum powders, in which the acid constituent is sulphuric acid obtained from alum.

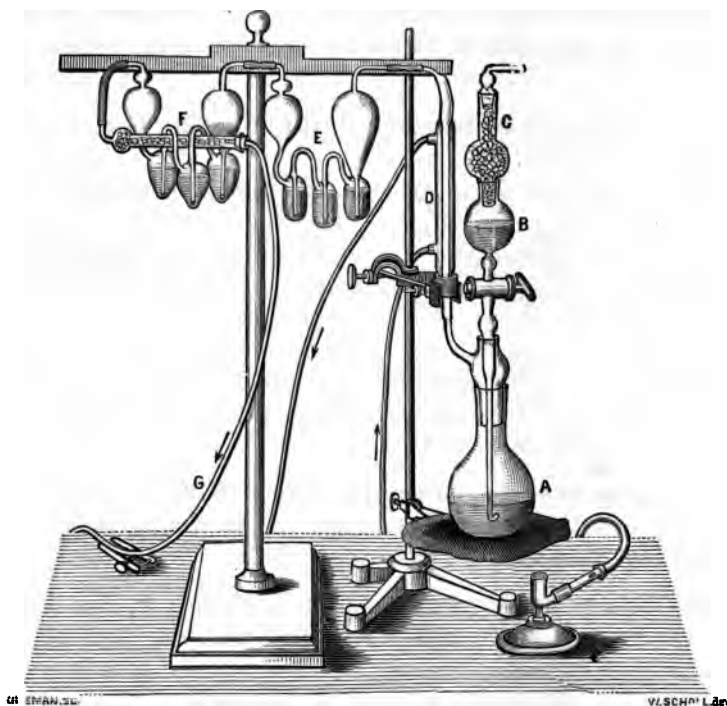
Besides these, there are sometimes mixtures of the above powders.

*Determination of Carbonic Acid.*—This is the most important part, since it determines the strength of the powder. The apparatus used is the one described by Knorr,\* and is shown in the following cut.

Two determinations are made—one for the total and the other for the available carbonic acid. The total carbonic acid is determined as follows : 1 or 2 gms. of the powder are placed in a weighed glass tube and weighed as quickly as possible. The

\*This Journal **3**, 162.





tube and its contents are gently dropped into the generating flask *A*, which must be perfectly dry, and the connections are made with the absorption apparatus and also with the funnel tube *B* which contains 10 cc. dilute sulphuric acid. The carbon dioxide is then liberated, collected and weighed in the usual manner. The available carbonic acid is determined in the same way by substituting distilled water for the dilute sulphuric acid. Prolonged boiling of the liquid residue is inadvisable, for if, through poor sampling, a considerable excess of bicarbonate is present, gas will be liberated from it and the result will be too high.

*Determination of Starch.*—"From 2 to 5 gms. are weighed out and transferred to an Erlenmeyer flask; to it are added about 150 to 200 cc. of a solution of hydrochloric acid, which has a strength of 4 per cent. of the acid gas.

The flask is provided with a cork perforated for the passage of

a condensing tube about 1 meter in length. The conversion is accomplished by gently boiling the acid liquid for four hours, after which the flask and contents are cooled, neutralized by the addition of sodium hydrate, made up to a definite volume, and the copper oxide reducing power determined. The latter operation is best carried out by the method in which asbestos-tipped filtering tubes are used for the end reaction. The reducing power being calculated as dextrose; 10 parts equal to 9 parts of anhydrous starch. To insure agreeing results, it is very essential to conduct the conversion under precisely the same conditions in all cases."

*Determination of Phosphoric Acid.*—2 gms. of the sample are ignited carefully in a muffle and treated with 30 cc. concentrated nitric acid. The method from this point is that used by the Association of Official Agricultural Chemists for total phosphoric acid in fertilizers.\*

*Determination of Tartaric Acid.*—In this the "Goldenberg Geroment"† method is used, modified to suit a tartrate baking powder.

"Weigh out 5 gms., wash into a 500 cc. flask with about 100 cc. water; add 15 cc. of strong hydrochloric acid; make up to mark and allow the starch to settle. Filter, measure out 50 cc. of the clear filtrate; add to it 10 cc. of a solution of carbonate of potash containing 300 gms.  $K_2CO_3$  to the liter and boil half an hour; filter into a porcelain dish and evaporate filtrate and washings to a bulk of about 10 cc. Add gradually with constant stirring 4 cc. glacial acetic acid and then 100 cc. 95 per cent. alcohol, stirring the liquid until the precipitate floating in it assumes a crystalline appearance. After it has stood long enough for this precipitate to form and settle, best for several hours, decant through a small filter, add alcohol to the precipitate, bring it on the filter, wash out the dish and finally the filter carefully, with alcohol, until it is entirely free from acetic acid. Transfer filter and precipitate to a beaker, add water, and boil, washing out the dish also with boiling water if any of the precipitate adheres to it. The resulting solution is titrated with decinormal

\*This Journal 2, 10.

†Chem. Zeit. 12, 390.

alkali solution, using phenol-phthalein as indicator; 1 cc. decinormal alkali solution corresponds to .0188 gm. of potassium bitartrate, or .015 gm. of tartaric acid."

*Determination of Alkalies.*—5 gms. of the sample are weighed out and ignited in a muffle at a low heat. The soda and potash were then determined according to the official methods\* for fertilizers, the mixture of the two chlorides being weighed before precipitating the potash with platinic chloride in order to determine the soda by difference.

*Determination of Aluminum.*—In the case of a pure alum powder, Allen's method for the quantitative estimation of alum in bread may be used with good results, but earthy phosphates are often found as impurities, and the following method for phosphate and alum powders is more accurate and more convenient.

"Weigh out 5 gms. into a platinum dish, char, treat with strong nitric acid, and filter into a 500 cc. flask. After washing the residue slightly, transfer filter and all back to the dish and burn to whiteness. To the ash add mixed carbonates and fuse. Take up with nitric acid, evaporate to dryness, acidify again with nitric acid, and wash all into the 500 cc. flask. Nearly neutralize the contents of the flask with ammonia, and add molybdate of ammonium sufficient to precipitate all the phosphoric acid present. Allow to stand some time, make up to the mark, shake thoroughly, and filter off 100 cc. through a dry filter. This is exactly neutralized with ammonia, keeping the solution as cool as possible to avoid the deposition of molybdic acid. Filter and wash the precipitate, redissolve in dilute nitric acid with the addition of a little ammonium nitrate, and precipitate as before. Filter through a paper filter, burn, ignite, and weigh as  $Al_2O_3$ . The alumina and phosphoric acid may be determined in the same sample by the above method, modifying it as follows:

When the solution, ash, etc., have all been brought into the graduated flask, make up to the mark without adding molybdate, filter, and take 100 cc., nearly neutralize with ammonia, add ammonium nitrate and molybdate of ammonium, digest and filter. The filtrate contains the aluminum, and may be precipitated with ammonia as above, while the phosphoric acid is all contained in

\*This Journal 2, 12.

the precipitate, which may be redissolved in ammonia and precipitated with magnesia mixture."

*Determination of Calcium.*—"Weigh out 5 gms. of the sample, transfer to a 500 cc. flask, add 40-50 cc. of water, and 20-30 cc. of strong hydrochloric acid. Make up to the mark with water, shake thoroughly, and set aside to allow the starch to settle. Filter through a dry filter, and take aliquot parts of the filtrate for precipitation; in phosphate powders not more than 50 cc. should be used. Nearly neutralize with ammonia, acidify slightly with acetic acid, add ammonium acetate, and boil. Filter from the precipitate, if there be any, add ammonium oxalate, and allow to stand several hours. Filter into a Gooch crucible, and dry at 100°. Weigh as oxalate."

*Determination of Sulphuric Acid.*—"Weigh out .5 to 1 gm. of the powder, and transfer to a beaker. Digest with strong hydrochloric acid until all of the powder, including the starch, goes into solution; add barium chloride to slight excess while still hot, and allow it to stand for twelve hours or over night. Filter, ignite, and weigh.

*Determination of Ammonia.*—This is present as bicarbonate, or as ammonium sulphate in the alum powders. In the latter case it may be calculated from the alumina and sulphuric acid already determined. In the former case it is determined by the Kjeldahl method as given in the official methods.\*

*Determination of Moisture.*—The most satisfactory way to obtain the water of association and combination is by difference. Other methods were tried and failed, and this no doubt is inaccurate for phosphate and alum powders. S. C.

**The Estimation of Para-Nitrotoluene.**—Frédéric Reverdin and Ch. de La Harpe, Chem. Zeit. 12, 787.

The method is based upon the fact that the sulphonic derivative of para-nitrotoluene is transformed by boiling with caustic soda into a derivative of stilbene (dinitrodisulphostilbene), the strongly alkaline solution being colored a deep red, while the sulphonated ortho-toluene is not attacked under the same conditions, the color of the solution remaining light yellow.

\*This method fully described in Bull. No. 19, U. S. Dept. of Agr.

For the determination it is necessary to have perfectly pure ortho-nitrotoluene, which is prepared as follows :

A mixture of 100 gms. of ortho-nitrotoluene of commerce, 25 gms. caustic soda, 25 gms. water and 50 gms. of alcohol is boiled for 24 hours in a flask supplied with a neck condenser. The solution is then diluted with water, rendered slightly acid, and distilled. About 70 gms. of nitrotoluene are obtained in the distillate, which is diluted and again distilled. About four-fifths of what passes over at first is collected. This contains about 40 gms. of nitrotoluene, and is distilled again without diluting, that part being collected which passes over at a constant temperature. The product thus obtained is perfectly free from para-nitrotoluene, as can be proved by using the reaction above referred to. 2 cc. of the pure ortho-nitrotoluene are placed in a test tube and heated with 6 cc. of sulphuric acid containing 25 per cent. of anhydride. The mixture is heated for three hours in an air bath, and is then poured out and diluted to one liter. In the same way a mixture of 96 per cent. of ortho-nitrotoluene and 4 per cent. of para-nitrotoluene is sulphonated and the product diluted to 200 cc. This solution is used as the standard, as commercial ortho-nitrotoluene contains about 4 per cent. of para-nitrotoluene, while at the same time this proportion produces a coloration well adapted for the determination. 1 cc. of this solution heated with 5 cc. of a 10 per cent. caustic soda solution gives a deep red coloration.

The determination is made by sulphonating the ortho-nitrotoluene to be examined in the same way as the standard and diluting to 200 cc. 1 cc. of each of the solutions is placed in a test tube, heated with 5 cc. of the caustic soda solution and the intensity of the coloration in each compared. If the specimen under examination shows a deeper coloration, a measured quantity, 20 or 50 cc., is taken and diluted with the solution of pure ortho-nitrotoluene above mentioned until the solution is of the same color as the standard. The number of cc. necessary to add in order to bring the 200 cc. of solution to the same coloration is then calculated and the percentage of para-nitrotoluene thus determined.

For mixtures containing less than 20 per cent. of para-nitrotoluene the error does not exceed .5 per cent., but if more than 20 per

cent. be present, the error is increased. The test tubes should be of the same size and the solutions heated simultaneously. I. A. P.

**Estimation of Fatty Acids in Alizarin Oil.**—Rowland Williams, Chem. News 61, 76.

The author questions the reliability of the method of Mr. Guthrie (Chem. News 61, 52, this Journal 4, 101). He doubts whether the sulpho-compounds are decomposed by heating with soda and then with a slight excess of sulphuric acid, and thinks that if a fatty acid, for example, sulpho-ricinoleic, were treated as described, sulpho-ricinoleic would be again liberated. Again, when the seller of alizarin oil guarantees 50 per cent. fatty acid, he means sulpho-fatty acids, while the discussed method would exclude them in the result. The insolubility of fatty acids in water is also considered contrary to experience, and a comparative analysis gave the following figures :

	Fatty Acids. Per cent.	
	Guthrie.	Williams.
No. 1 . . . . .	38.4	46.9
No. 2 . . . . .	44.3	50.8

while in an analysis of 75 per cent. oleine, the result was more than 12 per cent. too low, the solubility of the fatty acids being very apparent in this case.

A. H. W.

**Examination of Essential Oils by Maumene's Test.**—Rowland Williams, Chem. News 61, 64.

The test, in brief, consists in adding strong sulphuric acid to the oil under examination, generally in the case of ordinary fixed oils, in the proportion of 10 cc. of acid to 50 gms. of oil, both being at the same initial temperature (preferably 60° F.), stirring vigorously and noting the highest point indicated by the thermometer. To avoid loss of heat, the operation is conducted in a beaker, surrounded by cotton wool, packed in a large vessel. The test is but an arbitrary one, but the author's tabulated results may be interesting to those working in this field. The test, he thinks, may be useful as a confirmatory one, especially for the presence of rosin in cassia and other essential oils. When other methods have indicated the presence of that adulterant, the rise of temperature in the adulterated oils being much higher than in the case of the pure sample.

A. H. W.

**Test for Cotton-seed Oil in Lard.**—F. P. Perkins, *The Analyst* **15**, 51.

If .02 to .03 gm. of powdered potassium dichromate be mixed with a few drops of concentrated sulphuric acid in a porcelain dish and about .5 gm. of the sample added together with some water, the presence of cotton-seed oil will produce a green color after the mass has been stirred a few seconds, but if no cotton-seed oil is present, the yellow color of the dichromate will remain unchanged.

S. C.

**Rapid Estimation of Quinine in Medicine.**—Dr. Seaton and H. D. Richmond, *The Analyst* **15**, 42.

The ammonia and ether process being unsatisfactory for rapid work, the authors have found the following method to be sufficiently accurate to detect adulteration or any error in dispensing. It is based upon the facts that quinine bisulphate is neutral to methyl orange, while the base itself has no action on phenolphthalein.

“To 25 cc. of medicine add 2 drops of methyl orange (.25 gm. in 1 liter of water), and 2 drops of phenolphthalein (.5 gm. in 1 liter of 50 per cent. alcohol), titrate with  $\frac{n}{10}$  baryta solution until the free acid is all neutralized, which is shown by the red color just changing to a brown. Note the number of cc. used. Continue titration until the pink color of the phenolphthalein appears. Care must be taken not to overstep this last point, as the color does not develop immediately. The difference between the two titrations, multiplied by the factor .0218, gives the weight of the quinine sulphate (i. e., the 7 molecules of water hydrate) in gms. in the 25 cc. The number of cc. in the medicine prescribed is known, and the calculation becomes a simple proportion. The method is, of course, not applicable in the presence of salts, of which the base is precipitated baryta.”

The following results show the accuracy of the method :

	Volumetric.		Gravimetric.
1	21.2	•	20.8
2	23.4		23.2
3	16.5		16.1
4	20.3		20.0

Solutions of accurately prepared quinine were then tried, and

A.	12 gms. gave . . . . .	12.1	12.2	11.8	12.0
B.	20 " " . . . . .	19.7	19.9	19.9	19.7
C.	18 " " . . . . .	17.5	17.6	17.5	17.8
D.	15 " " . . . . .	15.4	14.7	14.9	15.2

S. C.

### Some Reactions of the Vegetable Oils with Silver Nitrate.

R. Brulle, Bull. soc. chim., 3d Series, 2, 208.

If 10 cc. of a vegetable oil and 5 cc. of fuming nitric acid are heated together in a porcelain capsule, a coloration is produced which is characteristic of the oil employed. If now there is added to this mixture 5 cc. of an alcoholic solution of silver nitrate—25 per cent of  $\text{AgNO}_3$  in alcohol at  $90^\circ$ —and the heating continued, at about  $115^\circ$  the silver nitrate decomposes and metallic silver is deposited on the sides of the capsules. The heating is continued until the first reflections produced by the metallic deposit have disappeared, and on tipping the capsule, there is observed the coloration of the thin oily layer which covers it, as well as the metallic reflections shining upon the surface of the liquid.

By this treatment different colorations are obtained, as is shown in the following table :

	Colorations Obtained.			
	Natural State.		Saponified.	
	Oily Layer.	Reflections.	Oily Layer.	Reflections.
Olive	Olive Green	Green	Mars Orange	Chypre Green
Cotton	Green	Ash Green	Burnt Sienna	Cobalt Violet
Sesamum	Chrome Green	Series Blue	Golden Yellow	Cobalt Violet
Arachide	Greenish Yellow	Emerald Green	Persian Lake	Bright Violet
Carnation	Olive Green	Bluish-Green	Ochre (Yellow)	Blue
Comelina	Persian Lake	Bright Blue	Deep Yellow	Blue
Linseed	Dragon Blood	Emerald Green	Black	Green
Rape-seed	Persian Lake	Chypre Green	Burnt Carmine*	Ultramarine

The names of the colors are those used in the *aquarelle*.

This method permits of the detection of the oils used to adulterate olive oil and of the determination of the amount present within 5 per cent.

I. A. P.

\*After cooling there are formed at the surface crystalline needles of a blue color.



## NEW BOOKS.

**Eyerman's Course in Determinative Mineralogy.\***—This is one of those books made necessary by reason of short time for the work to be done. It has been especially designed to fit the course as taught in Lafayette College. Such books have a great deal of value for the writer of them, and very often—when the conditions are the same—are useful to others as well. The author has gone over the ground carefully in an experimental way before writing his tables, and they should therefore be of great value, and an improvement upon those now in use. The course laid down is thoroughly practical, and is given in as few words as consistent with accuracy. The book is well worth examination by those who teach this subject.

E. H.

**Curtman's Chemical Reagents.†**—This book is likely to prove useful to those who have no access to libraries of chemical journals, or to those who having such a library have not time to look up the needful information. Besides the ordinary reagents given in most text books, those less commonly used—for example, cupric butyrate, flavescin, amido-dimethyl-aniline, etc., are given. Under each heading the uses, tests, and method of preparation of the reagent is given. It is to be expected that some errors should creep into such a compilation, and a few such occur. One great mistake has been made in not giving chapter and verse for at least most of the statements made, especially about the new and little known reagents. This would be a valuable addition, and we hope will be added in the next edition.

E. H.

\*A course in Determinative Mineralogy. By John Eyerman, of the American Geologist. Instructor in Lafayette College, Member of the Academy of Natural Sciences of Philadelphia, etc., etc., Easton, Pa. Published by the Author, 1890.

†Uses, Tests for Purity and Preparation of Chemical Reagents Employed in Qualitative, Quantitative, Volumetric, Docimastic, Microscopic and Petrographic Analysis, with a Supplement on the Use of the Spectroscope. By Chas. O. Curtman, M. D., Professor of Chemistry and Director of Chemical Laboratory in the Missouri Medical College. With 12 plates. St. Louis, Mo. John L. Boland Book and Stationery Co. 1890. Price, \$1.75.

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THE

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# Journal of Analytical Chemistry.

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## MILK ANALYSIS.

BY H. DROOP, RICHMOND.

Dr. Davenport and I are arguing at slightly cross purposes on this subject (*J. Anal. Chem.* IV, 26, 28). I do not wish to assert the superiority of ether as a solvent, nor to maintain that it is an essential part of the methods of fat extraction that I employed, but as I had used ether in my experiments, I wished to point out that it was sufficiently identical in solvent power with petroleum ether to render my results strictly comparable, and with the same intention I must take exception to Dr. Davenport's statement giving Henkel as authority that milk contains *citric acid soluble in ether*; Henkel does not state that it is free citric acid, and the researches of Söldner (*Landw. Versuch Stat.* 31, 351) show that it is all in the form of potassium and calcium citrates; Palm's researches have not only not been confirmed, but have had doubt cast upon them. I do not think, therefore, that the authorities quoted prove that there is any marked inferiority of ether. I propose, however, to make a series of comparative determinations with different solvents in order to settle this question.

But even were there something not milk-fat extracted by ether, I cannot admit that it vitiates my comparative experiments on the Adams, Kieselguhr, &c., methods on the one hand, and on Dr. Davenport's modification on the other, as in each case I employed ether, and it is surely unreasonable to suppose that in one case something should be dissolved and in the other not. The higher results obtained with the former processes are not due to mechanical impurities in the fat as weighed; a wad of cotton wool

of half an inch in thickness, such as I used, being sufficient to prevent any Kieselguhr being carried through, and I invariably tested my fats by dissolving them in ether and allowing any matter in suspension to settle. By this means very small quantities of Kieselguhr are detected, quantities which would not affect the percentage of fat in the second place of decimals. Whenever I detected Kieselguhr that had run through, which was not often, I did not take that result. I never found that Plaster of Paris ran through, and the papers used in the Adams' method gave merely a trace of loose fibres, never in extreme cases exceeding one milligram; moreover, I have obtained nearly the same weight of fat as given by the Adams and Kieselguhr processes by extracting the casein precipitated from the milk, well washed and dried in vacuo, and this weight was considerably higher than by Dr. Davenport's modification.

I think these facts show most conclusively that in Dr. Davenport's modification the whole of the fat is not extracted, and that the excess obtained by other methods is true milk-fat and does not consist of other substances dissolved by ether, and mechanical impurities.

KHEDIVIAL LABORATORY,  
CAIRO, EGYPT.

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CHEMICAL LABORATORY,  
DR. BENNETT F. DAVENPORT,  
161 TREMONT STREET.

BOSTON, MASS., June 7, 1890.

DR. E. HART—

*Dear Sir:* Many thanks for Dr. Richmond's proof, which I return. I do not know that I have anything further to say, since I, in the first place, upon page 311 of Vol. 3, claimed only that my method was "surely \* \* fine enough for all commercial work." Conducted as Dr. Richmond now says he does, I presume his results are more exactly accurate, and for scientific purposes therefore preferable. But for the commercial work and incidental information cast upon a milk, prosecuted for its marked deficiency in the required amount of *total* milk solids, I, having in the vicinity of 100 samples to examine in a day, much prefer my method of examination. For I could in no other way that I know of begin to get through with as many with equal accuracy. Truly, Dr. Richmond's method would probably involve as much time and labor.

Respectfully yours,

BENNETT F. DAVENPORT.

## TWO METHODS FOR THE DIRECT DETERMINATION OF CHLORINE IN MIXTURES OF ALKALINE CHLORIDES AND IODIDES.\*

BY F. A. GOOCH AND F. W. MAR.

The determination of chlorine associated with iodine in haloid salts is usually accomplished by differential or indirect means: either the two halogens are determined together in a portion of the assay while the iodine alone is estimated in a second portion by one or other of well known methods, the difference between the sum of the halogens and the iodine being the chlorine sought; or, the silver salts of the halogens are weighed together and then converted into a single salt, or the metal, the ratio of chloride to iodide in the original salt being found by simple algebraic processes. If the amounts of iodine involved are minute, it is possible to separate the element by Fresenius's method of treatment with nitrous acid and a solvent like carbon disulphide, and then to determine chlorine directly in the residue; but the manipulation of the process is difficult, and the results inaccurate, when much iodine must be removed. The only method which has been deemed generally applicable to the direct estimation of chlorine associated with iodine in haloid salts is based upon Lassaigne's reaction, by which the iodine is precipitated as palladious iodide; but, the necessity of removing the excess of palladium by hydrogen sulphide before proceeding to precipitate the chlorine is so irksome that, even in this process, it is found to be more convenient to fall back upon the estimation of chlorine as the difference between the iodine found by the palladium process and the sum of the iodine and chlorine obtained by another test in another portion of the material. A straightforward and easy method for determining the chlorine is obviously desirable, and in the work of which we here give an account we have endeavored to find such an one.

It is a well-known fact† that when an aqueous solution of hydrochloric acid is boiled a point of concentration is reached, by

\*From the *American Journal of Science*, Vol. XXXIX, April, 1890.

†Roscoe and Dittmar, *Quart. Jour. Chem.* xii, 128.

the excessive loss of acid from stronger solutions and of water from weaker ones, at which, for definite barometric pressure, the liquid boils at a constant temperature and distils unchanged in composition. It follows naturally that a degree of dilution may be reached beyond which the loss of the acid must be inappreciable. Indeed, Fleischer justifies his use of hydrochloric acid as a standard in alkalimetric processes upon his observation that decinormal solutions of this acid, and even solutions of twice the strength (7.3 gms. to the liter), do not yield after ten minutes' boiling enough acid to redden blue litmus paper held in the steam. Hydriodic acid behaves similarly to hydrochloric acid in the matter of volatilizing from aqueous solutions; but to the decomposing action of oxidizing agents it is far more sensitive. Our endeavor has been to find conditions under which hydriodic acid may be completely broken up, and its iodine removed from the solution by vaporization, while the hydrochloric is retained without appreciable loss. As a first step toward the solution of this question, we initiated a series of experiments upon the volatility of hydrochloric acid in solutions containing sulphuric acid, having fixed upon the latter as the most available means of liberating hydrochloric and hydriodic acids from their compounds with the alkaline metals. After a few preliminary experiments with litmus paper exposed in the steam from boiling solutions, we settled down upon two modes of investigating this point. According to the first, the determination of the chlorine remaining after concentration in solutions made up of water, sulphuric acid, and known amounts of the chloride, by precipitating as silver chloride, filtering the precipitate on asbestos, and weighing, was made the test of volatility of the hydrochloric acid; in the second, the same object was accomplished by estimating the chlorine escaping from the solution, by passing the steam through a condenser and precipitating the acid in the distillate by means of silver nitrate, collecting and weighing the silver chloride as in the former method.

The experiments of Series A to Series F were carried out according to the first method. In them portions of a dilute solution of potassium chloride of known value were measured from a burette into Erlenmeyer flasks of 500 cm.<sup>3</sup> capacity, sulphuric acid

diluted one-half was added, and the solution was boiled until the flask and contents removed from the flame and placed upon counterpoised scales just tipped the beam. A few trials sufficed to bring the weight to the required point, and the degree of concentration was determined by this means far more accurately than by lowering the level of the liquid to marks placed upon the flasks. The hydrochloric acid remaining after concentration was determined as described, the comparison of the result with the value of the standard solution of chloride indicating, of course, the total loss in the process.

In the experiments of Series A, B, C, D, the effect is traced of increasing proportions of chloride as compared with the same amount of sulphuric acid taken. In those of Series C, E, F, the influence of changing proportions of sulphuric acid, while the amount of chloride remains the same, is brought out. In both sets the evidence is plain that the volatility of the hydrochloric acid is dependent upon the proportion of the sulphuric acid as well as upon the amount of the chloride present. It appears likewise that when the amounts of sulphuric acid present are reasonably small the loss of hydrochloric acid is inconsiderable, if the concentration is not pushed to too great an extreme.

*Series A.*

Taken $\text{H}_2\text{SO}_4$ [cc].	Taken $\text{KCl}=\text{HCl}$ .		Found $\text{AgCl}=\text{HCl}$ .		Initial volume.	Final volume.	Error.
	gm.	gm.	gm.	gm.			
cm <sup>3</sup>					cm <sup>3</sup>	cm <sup>3</sup>	gm.
10	0.05	0.0245	0.0963	0.0245	110	65	0.0000
10	0.05	0.0245	0.0957	0.0243	110	45	0.0002—
10	0.05	0.0245	0.0945	0.0240	110	40	0.0005—
10	0.05	0.0245	0.0941	0.0239	110	35	0.0006—
10	0.05	0.0245	0.0871	0.0221	110	30	0.0024—
10	0.05	0.0245	0.0821	0.0209	110	25	0.0036—

*Series B.*

10	0.1	0.0489	0.1910	0.0485	110	65	0.0004—
10	0.1	0.0489	0.1922	0.0488	110	55	0.0001—
10	0.1	0.0489	0.1908	0.0485	110	45	0.0004—
10	0.1	0.0489	0.1894	0.0482	110	35	0.0007—

*Series C.*

Taken $\text{H}_2\text{SO}_4$ [1:1].	Taken $\text{KCl}=\text{HCl}$ .		Found $\text{AgCl}=\text{HCl}$ .		Initial volume.	Final volume.	Error.
10	0.2	0.0978	0.3837	0.0976	110	75	0.0002—
10	0.2	0.0978	0.3838	0.0976	110	65	0.0002—
10	0.2	0.0978	0.3831	0.0974	110	55	0.0004—
10	0.2	0.0978	0.3816	0.0970	110	45	0.0008—
10	0.2	0.0978	0.3746	0.0953	110	35	0.0025—
10	0.2	0.0978	0.3322	0.0845	110	25	0.0133—

*Series D.*

$\text{cm}^3$	gm.	gm.	gm.	gm.	$\text{cm}^3$	$\text{cm}^3$	gm.
10	0.4	0.1956	0.7690	0.1955	110	60	0.0001—
10	0.4	0.1956	0.7682	0.1954	110	50	0.0002—
10	0.4	0.1956	0.7574	0.1926	110	35	0.0030—

*Series E.*

5	0.2	0.0978	0.3845	0.0978	105	55	0.0000
5	0.2	0.0978	0.3838	0.0976	105	45	0.0002—
5	0.2	0.0978	0.3823	0.0972	105	35	0.0006—
5	0.2	0.0978	0.3788	0.0963	105	25	0.0015—

*Series F.*

20	0.2	0.0978	0.3782	0.0962	120	75	0.0016—
20	0.2	0.0978	0.3602	0.0916	120	65	0.0062—
20	0.2	0.0978	0.3087	0.0785	120	55	0.0193—
20	0.1	0.0978	0.2931	0.0745	120	45	0.0233—

The quantities of chloride dealt with in the preceding experiments are rather smaller than those which would naturally be handled in practical analysis, so that it seemed best to extend the experimentation to solutions of greater dilutions and containing larger amounts of chloride. In the experiments of Series G, and subsequently, the second mode of treatment referred to was adopted. The flask was filled as before, but was connected with an ordinary glass condenser so that the distillate might be collected and measured, and the hydrochloric acid condensed with the steam was estimated by precipitation as silver chloride, the last being dried and weighed as such upon asbestos. The details of the experiments are given in the tabular statement.

*Series G.*

Taken $\text{H}_2\text{SO}_4$ [1:1].	Taken $\text{KCl}=\text{HCl}$ .		Initial volume.	Final volume.	Time in minutes.	Found $\text{AgCl}$ .	Loss of $\text{HCl}$ .
$\text{cm}^3$	gm.	gm.	$\text{cm}^3$	$\text{cm}^3$		gm.	gm.
10	1	0.4888	400	300	29	0.0005	0.0001
10	1	0.4888	400	300	22	0.0008	0.0002
10	1	0.4888	350	300	10	0.0004	0.0001
10	1	0.4888	350	300	9	0.0005	0.0001
10	1	0.4888	300	200	25	0.0008	0.0002
10	1	0.4888	200	100	27	0.0021	0.0005
10	1	0.4888	100	50	20	0.0037	0.0009

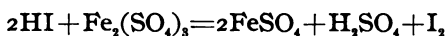
It is obvious from these results that a solution containing 10  $\text{cm}^3$  of the 1 : 1 sulphuric acid, or 5  $\text{cm}^3$  of the strong acid, may be concentrated to 200  $\text{cm}^3$  without significant loss of hydrochloric acid. At a concentration of 100  $\text{cm}^3$  the loss is notable. In later experiments, we found that a small part of the precipitate which we weighed in these experiments must in reality have resulted from the action of the solution upon the rubber stopper and connectors of the apparatus; for the distillate from pure water in the apparatus yielded a precipitate, probably silver sulphide, which filtered off and weighed, was found to amount to 0.0003 gm. The figures of Series G, therefore, overstate somewhat the volatility of hydrochloric acid under the circumstances, but the misrepresentation is inconsiderable. We fixed upon 300  $\text{cm}^3$  as a convenient volume of liquid to manipulate in future experiments, and one sufficiently dilute to guarantee security against the volatilization of hydrochloric acid when the amount of sulphuric acid does not exceed 5  $\text{cm}^3$  of the strong acid, and when the quantity of potassium chloride present does not exceed 1 gm.

The next point to be considered was the proper mode of breaking up hydrochloric acid and volatilizing the iodine thus set free, while leaving the hydrochloric acid fixed.

The use of dihydrogen potassium arseniate, which has been utilized to liberate iodine according to a method recently developed in this laboratory,\* is precluded by the necessarily high degree of dilution of the solution employed. The first trials were made, therefore, with ferric alum to act as the oxidizing agent according to the well known reaction of Duflos :

\*Gooch and Browning, this Journal, vol. 4, 124.





We found by experiment that from a volume of 300 cm<sup>3</sup> containing 10 cm<sup>3</sup> of sulphuric acid [1:1], 5 gms. of ferric alum, and 0.005 grm. of potassic iodide, every trace of iodine had disappeared so completely after five minutes' boiling that nitrous acid and chloroform collected no color in the cooled liquid. It transpired, however, that when the amount of potassium iodide was increased to 1 grm., iodine was found in considerable amount after boiling for an hour with occasional replacing of the water evaporated, so that the volume should not decrease much below 300 cm<sup>3</sup>. The failure of the iron alum to expel the iodine is not attributable to a deficiency in amount; for the 5 gm. present were capable of decomposing more than a gram and a half of potassium iodide were the full effect theoretically possible attained. Furthermore, special tests in which the amount of ferric alum was increased developed the fact that the increase was but little helpful. The apparent explanation of the phenomenon is that here, as in the liberation of iodine by means of dihydrogen potassium arseniate, there occurs a time in the course of action when for a given degree of dilution an equilibrium is established between the tendency of the oxidizer to oxidize and that of the reduced residue to reverse the action. The obvious modes of securing completed action are the concentrating of the liquid and the reinforcing of the oxidizer. Application of the former is precluded by the danger of volatilizing hydrochloric acid; the simplest mode of realizing the latter—and as the result proved, a feasible one—is the re-oxidation of the reduced ferrous sulphate by means of nitric acid.

When a sufficient amount of nitric acid is added to restore the iron to the ferric state, the boiling of the solution resulted in the complete liberation of the iodine. In dilute solutions the amount of nitric acid necessary to oxidize a fixed quantity of ferrous salt is greater than in concentrated solutions. Thus, while 0.1 cm<sup>3</sup> of strong nitric acid should be more than enough to reoxidize the iron reduced by 1 gm. of potassium iodide when the full oxidizing action is brought out, we found it necessary to add to the dilute solutions with which we worked about 2 cm<sup>3</sup> of the acid to complete the action satisfactorily. Incidentally, we found that the nitric acid by itself—that is, without the presence of the iron salt

—is not effective in liberating the iodine ; for, the successive addition of portions of 1 cm<sup>3</sup> of nitric acid to a solution containing 10 cm<sup>3</sup> of sulphuric acid [1 : 1], and 1 gm. of potassium iodide in a total volume of 400 cm<sup>3</sup> until the amount of nitric acid reached 5 cm<sup>3</sup>, the liquid boiling all the time, liberated but little iodine, while the addition at this point of 2.5 gm. of ferric alum determined the evolution of iodine in dense fumes.

*Series H.*

Taken H <sub>2</sub> SO <sub>4</sub> [1:1].	Taken Iron Alum.	Taken HNO <sub>3</sub> Sp. Gr. 1.40.	Taken KCl=HCl.		Initial volume.	Final volume	Time in min- utes.	Found AgCl.	Loss of HCl.
gm.	gm.	cm <sup>3</sup>	gm	gm.	cm <sup>3</sup>	cm <sup>3</sup>		gm.	gm.
...	...	1	1	0.4888	200	100	30	0.0006	0.0002
...	...	1	1	0.4888	100	50	14	0.0010	0.0003
...	...	1	1	0.4888	50	15	10	0.0049	0.0012
10	...	1	1	0.4888	200	100	27	0.0031	0.0008
10	...	1	1	0.4888	100	50	16	0.0116	0.0029
10	5	0.1	1	0.4888	400	300	24	0.0004	0.0001
10	5	0.3	1	0.4888	400	300	30	0.0004	0.0001
10	5	0.5	1	0.4888	400	300	30	0.0004	0.0001
10	5	1	1	0.4888	400	300	27	0.0010	0.0003
10	5	1	1	0.4888	300	200	33	0.0007	0.0002
10	5	1	1	0.4888	200	100	30	0.0025	0.0006
10	5	1	1	0.4888	100	50	15	0.0090	0.0023
10	5	2	1	0.4888	400	300	25	0.0010	0.0003
10	5	3	1	0.4888	400	300	25	0.0010	0.0003
10	5	4	1	0.4888	400	300	30	0.0009	0.0002
10	5	5	1	0.4888	400	300	30	0.0007	0.0002
10	5	10	1	0.4888	400	300	30	0.0018	0.0005

The addition of 2 cm<sup>3</sup>, or at the most 3 cm<sup>3</sup>, of strong nitric acid to solutions constituted as has been described proved to be sufficient to liberate the entire amount of iodine present. The question as to whether the hydrochloric acid is affected by the addition of so much nitric acid was settled in the experiments of the following series. In these determinations a little sulphurous acid was added to each distillate to insure the complete precipitation of the chlorine by silver nitrate, and sufficient nitric acid was added to re-dissolve the silver sulphite thrown down also at first.

It appears in these results that the ferric salt has no perceptible influence upon the hydrochloric acid, and that the presence of nitric acid within reasonable limits does not sensibly increase the loss of hydrochloric acid which takes place under conditions otherwise similar, strong nitric acid to the amount of 5 cm<sup>3</sup> in a

total volume of 300 cm<sup>3</sup> producing no apparent increment of loss from half a gram of hydrochloric acid. The nitric acid itself passes easily into the distillate. That the influence of the sulphuric acid is important, is again demonstrated in the experiments in which 1 cm<sup>3</sup> of nitric acid and 1 gm. of potassium chloride were distilled in the one case with, and in the other without, the addition of sulphuric acid.

In the indication of these and previous experiments we found warrant for the prosecution of the quantitative tests of the following series :

Weighed portions of a standard solution of potassium chloride (whose value was determined by precipitating with silver nitrate with the usual precautions, collecting in a perforated crucible upon asbestos felt the silver chloride found, and drying and weighing it) were transferred to Erlenmeyer flasks of 500 cm<sup>3</sup> capacity, water was added with 10 cm<sup>3</sup> of sulphuric acid [1 : 1], 2 gm. of ferric sulphate (either in the form of iron alum or an equivalent amount of ferrous sulphate oxidized in concentrated solution with a sufficiency (0.3 cm<sup>3</sup> of nitric acid) and 1 gm. of potassium iodide, were introduced, the whole volume was brought to 400 cm<sup>3</sup>, and the liquid was boiled with the addition of nitric acid as indicated in the table, 1 cm<sup>3</sup> being added after it appeared that all iodine had been expelled.

The color of the ferric salt renders it impossible to tell by the appearance of the solution the exact moment when the iodine has been expelled, and starch paper loses its sensitiveness in hot vapors. We bestowed some attention, therefore, upon means for the detection of small amounts of iodine in hot steam in order to avoid the inconvenience of condensing the distillate and testing it for iodine. We found that red litmus, preferably wet, is a most sensitive agent for the detection of iodine under the circumstances, taking on with exposure to traces of the vapor carrying that element, a distinct gray blue, deepening with exposure to larger amounts into a lavender blue. The addition of 0.005 gm. of iodine to 400 cm<sup>3</sup> of boiling water produces immediately upon red litmus paper the characteristic lavender blue color, and the test grows fainter and fainter as fresh test-papers are exposed, until at the end of five minutes, or thereabouts, when the litmus paper shows

no color, the cooled solution yields no iodine to nitrous acid and chloroform. This reaction of litmus we found of great value and in no case in which an exposure of two minutes' duration failed to develop the characteristic color were we able to find iodine in the cooled liquid. To prevent mechanical loss of liquid we made use of the trap described in a previous paper from this laboratory, consisting simply of an ordinary two bulb straight drying tube cut off short and hung with the large end downward in the mouth of the Erlenmeyer flask. The residue in the flask after the expulsion of the iodine was treated with silver nitrate, and the precipitated chloride was determined similarly to that obtained in standardizing the solution of potassium chloride.

*Series I.*

$\text{H}_2\text{SO}_4$ [i.].	$\text{Fe}_2(\text{SO}_4)_3$	$\text{HNO}_3$	$\text{KCl}=\text{HCl}$		$\text{KI}$	Initial volume.	Final volume.	Time in Minutes.	$\text{AgCl}=\text{HCl}$ found. found.		Error.
			gm.	gm.	gm.				gm.	gm.	
cm <sup>3</sup>	gm	cm	gm.	gm.	gm	cm <sup>3</sup>	cm <sup>3</sup>		gm.	gm.	gm.
10	2*	.	0.4960	0.2425	.	400	300	40	0.9536	0.2425	0.0000
10	2*	.	0.4970	0.2429	.	400	300	40	0.9534	0.2624	0.0005—
10	2*	.	0.4942	0.2416	.	400	300	30	0.9509	0.2418	0.0002+
10	2*	2	0.4969	0.2429	.	400	300	30	0.9559	0.2431	0.0002+
10	2*	3	0.4956	0.2423	†	400	350	30	0.9546	0.2428	0.0005+
10	2*	3	0.4969	0.2429	†	400	350	23	0.9662	0.2432	0.0003+
10	2†	3	0.4949	0.2419	†	400	300	27	0.9523	0.2422	0.0003+
10	2†	5	0.4970	0.2429	†	400	250	55	0.9559	0.2431	0.0002+
10	2†	5	0.4955	0.2422	†	400	300	30	0.9524	0.2422	0.0000
10	2†	5	0.4967	0.2428	†	400	300	33	0.9546	0.2428	0.0000
10	2†	6	0.4964	0.2427	†	400	300	30	0.9550	0.2429	0.0002+

Several determinations in blank—that is, experiments from which the iodine was purposely omitted—are included, for the sake of comparison, in the tabular statement.

These eminently satisfactory results prove the trustworthiness of the method.

The fact that nitric acid appears to affect so little the hydrochloric acid in the solution, suggested the possibility that nitrous acid itself might be turned to account and used in a similar process instead of a ferric salt and nitric acid. Some preliminary experiments were made, therefore, to test the behavior of hydro-

\*The iron was added in the form of iron alum.

†The iron was added as  $\text{FeSO}_4$  oxidized by  $\text{HNO}_3$ .

chloric acid under the action of nitrous acid, and, as they gave favorable indications, the experiments of Series J were undertaken to test the action quantitatively. The general conduct of the test was similar to that followed in Series I. The solution of chloride and iodide containing 10 cm<sup>3</sup> of sulphuric acid [1 : 1] was diluted to 400 cm<sup>3</sup>, and agitated while the gas developed by the action of sulphuric acid on 2 gm. of sodium nitrite was passed into it. With pure sodium nitrite at hand there is probably no serious objection to introducing that substance directly into the solution, but impurities in the article at our disposal made it desirable to generate the gas outside the solution.

For a generator we used two straight drying tubes connected by a rubber tube and set up after the fashion of the von Babo generator, and regulated the rapidity of the current to a rate of five or six bubbles to the second by changing the relative elevation of the generator tubes. The iodine separates immediately upon the introduction of the nitrous fumes and escapes upon boiling in dense fumes, leaving the solution colorless in a very short time. The litmus test was applied as an additional safeguard to indicate the completion of the removal of the iodine. The results of the experiments as given in the accompanying table are evidently satisfactory.

*Series J.*

H <sub>2</sub> SO <sub>4</sub> [1:1].	NaNO <sub>2</sub> used in generator.	KCl=HCl.		KI.	Initial volume.	Final volume.	Time in minutes.	AgCl=HCl. found. found.		Error.
		gm.	gm.					gm.	gm.	
cm <sup>3</sup>	gm.			gm.	cm <sup>3</sup>	cm <sup>3</sup>				
10	2	0.4953	0.2421	1	400	350	20	0.9524	0.2422	0.0001+
10	2	0.4975	0.2432	1	400	350	16	0.9573	0.2434	0.0002+
10	2	0.4956	0.2423	1	300	250	15	0.9530	0.2423	0.0000
10	2	0.4973	0.2431	1	300	250	15	0.9550	0.2429	0.0002—
10	2	0.4964	0.2427	1	300	250	15	0.9550	0.2429	0.0002+
10	2	0.4969	0.2429	1	300	250	15	0.9567	0.2433	0.0004+

The modes of proceeding to the separation of iodine and the estimation of chlorine according to the processes which we have detailed may be briefly summarized as follows :

*First Method.*—To the solution of the alkaline chloride and iodide diluted to about 400 cm<sup>3</sup> in an Erlenmeyer flask capable of

containing a liter, are added 10 cm<sup>3</sup> of sulphuric acid of half strength, with 2 gms. of ferric sulphate (either in the form of iron alum, or ferrous sulphate oxidized in concentrated solution by about 0.3 cm<sup>3</sup> of nitric acid), and 3 cm<sup>3</sup> of nitric acid. A trap, of the form described, is hung in the neck of the flask, and the liquid is boiled until the steam which escapes no longer gives to red litmus paper, after two minutes' exposure, the characteristic gray blue due to traces of iodine. Then 1 cm<sup>3</sup> more of nitric acid is added, and the test for iodine again made. When no iodine is found in the escaping vapor, silver nitrate is added in excess to the contents of the flask, the precipitate is settled, collected in a perforated crucible on asbestos, dried, and weighed as silver chloride.

*Second Method.*—The solution of the chloride and iodide contained in an Erlenmeyer flask is diluted to 400 cm<sup>3</sup>; 10 cm<sup>3</sup> of sulphuric acid of half strength are added, and the vapor from 2 gms. of sodium nitrite acted upon by dilute sulphuric acid (preferably in a simple generator, such as is described above) is passed with reasonable rapidity into the agitated solution. The liquid is boiled until colorless, and still further until litmus paper placed in the steam gives no reaction for iodine after an exposure of two minutes. The contents of the flask are treated with silver nitrate, and the precipitated chloride is treated exactly as in the first method.

Both methods are convenient and precise.

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## STUDY OF A METHOD FOR THE QUANTITATIVE DETERMINATION OF SUCROSE, INVERT SUGAR AND DEXTROSE, OR LEVULOSE.\*

BY F. G. WIECHMANN, PH. D.

### PART I.

The quantitative determination of sucrose, invert sugar and dextrose, or levulose, when these substances occur together, presents a problem of considerable interest and importance.

Winter† suggested a method of separating sucrose from dextrose and levulose, and dextrose from levulose. It consists in adding

\*School of Mines Quarterly, No. 3, Vol. XI.

†Zeitschrift des Vereins für Rübenzucker-industrie, 1888, vol. xxxviii, page 782.

ammoniacal acetate of lead,\* made immediately before use, to the solution of the sugars, until there is no further precipitation. The precipitate, which is ordinarily of a dazzling white color, is digested with a great amount of water, and then filtered.

The filtrate contains the sucrose as a lead compound. Decompose this compound by carbonic acid gas, and filter off the carbonate of lead. The solution then contains the sucrose.

Wash the residue thoroughly with water, then suspend it in water and saturate with carbonic acid gas. This gives a filtrate and a residue. The filtrate contains the dextrose. The precipitate consists of carbonate of lead and of a compound of lead with levulose. Wash well with water, then suspend the precipitate in water and pass in sulphuretted hydrogen. The precipitated sulphide of lead is filtered out, washed thoroughly, and the filtrate, to which the washings have been added, is concentrated on a water-bath, and the levulose in it determined.

This method aims at the actual separation of the sucrose, the dextrose and the levulose, and thus, of course, permits of the separate determination of each constituent. But even if this method were perfectly satisfactory and reliable, which the writer, from his experiments, is strongly inclined to question, even then it would hardly prove a desirable method for an analytical determination on account of the time required for its execution.

Other attempts to determine levulose and dextrose when in combination, have been made. These are, however, based either entirely or partially on optical analysis.

As, however, fluctuations of temperature affect to a marked degree polariscopic determinations of inverted sugar solutions (invert sugar, levulose), it seemed to the writer that a method which should be entirely independent of optical analysis, and be based wholly on data obtained by gravimetric methods, would be the most desirable.

Tollens, in his *Kurzes Handbuch der Kohlenhydrate*, 1888, makes the following statement :

“ If levulose is mixed with dextrose, or with any other glycoses less sensitive to acids, the sum of the glycoses may be determined with Fehling’s solution. Then the levulose may be destroyed by

\*Add ammonia to acetate of lead as long as the precipitate just continues to disappear.

hydrochloric acid, according to Sieben's directions, and, after neutralizing by sodic hydrate, the remaining dextrose may be determined, and the difference calculated as levulose."

If a reliable process could be based on this suggestion, it would prove a simple and rapid method for the estimation of the sugars named, when occurring together.

In the following pages there will be described a course of analysis, and the methods of calculation deemed necessary to attain the desired result.

The estimations to be made consist of the following :

1. Total sucrose.
2. Total reducing sugars.
3. Dextrose, after destruction of the levulose by Sieben's method.

For the tables expressing the relation between the copper precipitated and the sucrose, the invert sugar, the dextrose and levulose respectively, reference must be made to the memoirs cited.

The Fehling solution, used in all of the following determinations, has consisted of :

Sulphate of copper, crystallized, 34.639 gms. in 500 cc. of water.

Rochelle salts, crystallized, 173. gms. in 400 cc. of water.

Sodic hydrate, crystallized, 50. gms. in 100 cc. of water.

#### I. DETERMINATION OF TOTAL SUCROSE.\*

Weigh out 13.024 grams of sample. Dissolve with about 75 cc. of water in a 100 cc. flask.† Add 5 cc. hydrochloric acid containing 38 per cent. HCl (specific gravity, 1.188). Heat for two or three minutes on a water-bath up to between 67° and 70° C. Then keep at this temperature (as close to 69° C. as possible) for five minutes, with constant agitation. Cool quickly and make up to 100 cc. Remove 50 cc. by a pipette, place in a liter flask, and fill up to 1000 cc. Of this solution take 25 cc. (corresponding to 0.1628 gm. of sample), neutralize the free acid present by 25 cc. of a solution of sodium carbonate, prepared by dissolving 1.7 gms. of crystallized sodium carbonate in 1000 cc. of water.

\*German Government Method. See Die Deutsche Zuckerindustrie, 1888. Besondere Beilage zu No. 27.

†Do not add any basic acetate of lead for clarifying purpose, as this will introduce a source of error, and yield results too low.



Then add 50 cc. of Fehling's solution, heat to boiling as directed in determination of total reducing sugars, and boil for three minutes.

## II. TOTAL REDUCING SUGARS.\*

Weigh out 26.048 gms. Place in a 100 cc. flask, clarify with basic acetate of lead, make up to 100 cc., filter and polarize. Take an aliquot part of the filtrate, add sodium sulphate to remove any lead present, make up to a definite volume and filter. It is best to arrange the dilution so that the 50 cc. of this filtrate, which are to be used for the determination of the total reducing sugar, will precipitate between 200 and 300 mgs. of copper.

To 50 cc. of the sugar solution prepared as above, add 50 cc. Fehling's solution (25 cc. copper sulphate and 25 cc. of Rochelle salt-soda solution).

Over the wire gauze above the flame lay a sheet of asbestos, provided with a circular opening of about 6.5 cm. diameter; on this place the flask, and arrange the burner in such a manner that about four minutes are consumed in heating the solution to the boiling-point. From the time that the solution starts to boil,—the moment when bubbles arise not only from the centre but also from the side of the vessel,—continue to boil for exactly two minutes, with a small flame. Then remove the flask from the flame immediately, and add 100 cc. cold distilled water from which the air has previously been removed by boiling.†

Then filter through an asbestos filter, wash and reduce to metallic copper.

This operation is carried out in the following manner: Clean thoroughly a small straight calcium chloride tube, or any other tube of similar pattern. Introduce asbestos fibers‡ so as to fill about half of the bulb. Draw air through while drying, cool and weigh. Connect with aspirator, filter the precipitated  $\text{Cu}_2\text{O}$ , wash with hot water, then, having changed the receiving flask, wash twice with absolute alcohol and twice with ether. Having removed the greater part of the ether by an air current, connect

\*School of Mines Quarterly, vol. ix., No. 1, 1888.

†The water is added to prevent subsequent precipitation of cuprous oxide.

‡The asbestos must first be prepared by washing successively with a solution of caustic soda (not too concentrated), boiling water, nitric acid, and again with boiling water. When filled into the glass tube, the asbestos is made to rest on a perforated platinum cone.

the upper part of the filter tube by means of a cork and some glass tubing with a hydrogen apparatus, and heat with a small flame, whose tip is about 5 cm. below the bulb containing the  $\text{Cu}_2\text{O}$ . The reduction in the current of hydrogen gas is finished in two or three minutes.

After the asbestos-tube has been cooled in the current of hydrogen, air is drawn through and the tube is then weighed.

After an analysis is completed, the asbestos is readily freed from the adhering copper by washing with dilute nitric acid.

### III. DEXTROSE BY ALLIHN'S METHOD.\*

Take 30 cc. copper sulphate solution, 30 cc. Rochelle salt-soda solution,† 60 cc. water. Heat to boiling. Then add 25 cc. of the solution to be tested, which must, however, not contain more than 1 per cent. of the active substance, and boil for two minutes. Then proceed as before, filtering, reducing the cuprous oxide, etc.

### IV. LEVULOSE BY LEHMANN'S METHOD.‡

Take 25 cc. of copper sulphate solution, 25 cc. Rochelle salt-soda solution,§ 50 cc. water. Heat to boiling. Then add 25 cc. levulose solution, which must not containing more than 1 per cent. of the active substance. Boil for 15 minutes, and proceed as previously directed.

### SIEBEN'S METHOD FOR DESTRUCTION OF LEVULOSE.||

Take 100 cc. of a solution made to contain 2.5 gms. of the dry substance (invert sugar, or invert sugar and levulose), place in a flask, add 60 cc. six times normal strength  $\text{HCl}$ , and heat in a boiling water-bath for three hours. Cool immediately, neutralize with six times normal strength  $\text{NaOH}$  solution, make up to 250 cc. and filter. Of the filtrate, use 25 cc. to determine dextrose according to Allihn.

The calculation of the results obtained by these methods here described is effected as follows :

\*E. Wein, Tabellen zur Quantitativen Bestimmung der Zuckerarten, 1888.

†173 gms. Rochelle salts and 125 gms. potassic hydrate are dissolved in water and made up to 500 cc.

‡E. Wein, Tabellen zur Quantitativen Bestimmung der Zuckerarten, 1888.

§Prepared by dissolving 345 gms. Rochelle salts and 250 gms. sodic hydrate in water, and making up to 1 liter.

||Zeitschrift des Vereines für Rübenzucker-industrie, vol. xxxiv, p. 869.

*Calculation.*

The calculation consists of two steps. Step 1 is always the same, and merely establishes whether the dextrose and the levulose are present in the proportion of 1:1, or whether either is in excess. Step 2 determines the amount of this excess, be it of dextrose or of levulose.

The values analytically determined are :

No. 1 = Cu reduced by total sucrose + total reducing sugars.

No. 2 = Cu reduced by total reducing sugars.

No. 3 = Cu reduced by dextrose (after Sieben's treatment).

*Step 1.*—No. 1 is Cu reduced by inverted sucrose + total reducing sugars. No. 2 is Cu reduced by total reducing sugars.

No. 1 minus No. 2 is Cu reduced by inverted sucrose. Report the corresponding value as sucrose. The difference between No. 1 and No. 2, divided by 2, represents the Cu reduced by the dextrose of the inverted sucrose. Call this value  $x$ .

No. 3 is Cu reduced by total dextrose (after Sieben's treatment.)  $x$  is Cu reduced by the dextrose of the inverted sucrose.

No. 3 less  $x$  is Cu reduced by the dextrose of the total reducing sugars. Call this value  $y$ .

$y \times 2 = 2y$ . Cu reduced by invert sugar + free dextrose, if any be present. Compare this value,  $2y$ , with No. 2.

If  $2y =$  No. 2, invert sugar *only* is present. If so, report as invert sugar.

If  $2y >$  No. 2 free dextrose is present.

If  $2y <$  No. 2 free levulose is present.

*Step 2.*—When  $2y >$  No. 2. Free dextrose is present.

No. 2 is Cu reduced by total reducing sugars.  $y =$  Cu reduced by the dextrose from the total reducing sugars.

No. 2 minus  $y =$  Cu reduced by the levulose of the total reducing sugars. Call this value  $p$ .

$p \times 2 = 2p =$  Cu reduced by invert sugar. Report as invert sugar.

No. 2 is Cu reduced by total reducing sugars.  $2p =$  Cu reduced by invert sugar.

No. 2 minus  $2p =$  Cu reduced by free dextrose.

*Step 2.*—When  $2y < \text{No. 2}$ . Free levulose is present.

No. 2 is Cu reduced by the total reducing sugars.  $2y = \text{Cu}$  reduced by invert sugar. Report as invert sugar.

No. 2 minus  $2y = \text{Cu}$  reduced by the free levulose.

In these calculations no attention has been paid to the fact that the reducing power of invert sugar, dextrose and levulose is not identical. The reducing power of dextrose being considered as 100, that of invert sugar is 96, and that of levulose is 94.\*

For very accurate work, the necessary corrections for these variations must be made.

In order to test the applicability of the method here described for determining invert sugar, dextrose and levulose, the following experiments were carried out :

Four series of experiments were made, embracing, respectively, mixtures of :

- I. Invert sugar and dextrose.
- II. Invert sugar and levulose.
- III. Sucrose, invert sugar and dextrose.
- IV. Sucrose, invert sugar and levulose.

Of course, from the very nature of the test, the sucrose becomes inverted, and so really Series III and IV, as well as I and II, are only mixtures of invert sugar and dextrose, or of invert sugar and levulose ; but the proportions between the invert sugar and the dextrose, or the levulose, respectively in Series III and IV, have been so arranged as to approximately correspond to the composition of certain raw sugars.

The dextrose used in the following experiments was anhydrous crystallized dextrose, prepared under the Behr patent.

The levulose was prepared under the writer's directions in the following manner :

Inulin . . . . .	18 gms.
Sulphuric acid (sp. gr. 1.840) . . . . .	36 cc.
Water . . . . .	516 "

This solution was set aside for nine days, then just neutralized with barium hydrate, filtered, and the filtrate evaporated to a solution having a density of 1.0043.

\*Soxhlet, *Journal für praktische Chemie*, vol. xxi, pp. 289 and 290.

The levulose solution was examined by the polariscope, and tested with Fehling's solution, and was found by both tests to possess the properties of chemically pure levulose.

The invert sugar solution was prepared by dissolving 13.024 gms. of chemically pure sugar (sucrose) in about 75 cc. water, adding 5 cc. hydrochloric acid, and heating in a water-bath up to between 67° C. and 70° C. When the contents of the flask had attained this temperature, they were kept at this point for five minutes more with frequent agitation. Then the contents of the flask, after having been cooled down to 17.5° C., were made up to 100 cc. with distilled water.

50 cc. of this solution were removed, placed in a liter flask, and made up to 1000 cc.

25 cc. of this solution correspond to 0.1528 gm. dry substance.

This amount, or whatever amount be taken for the analytical determination, must, before mixing with the copper solution, be neutralized by a solution of sodium carbonate, which is prepared by dissolving 1.7 gms. of the anhydrous salt in 1 liter of water.

A preliminary test made of the Sieben process on pure invert sugar was the following :

Placed 25.0 gms. granulated sugar in 1 liter of water. Of this solution took 50 cc., added 5 cc. concentrated hydrochloric acid, and made up to 100 cc. Heated for five minutes between 67° and 69° C., cooled, neutralized with sodium carbonate, and made up to 500 cc. Of this solution 5 cc. = 0.125 gms. dry substance, were used for the determination.

This gave before Sieben's treatment . . . . .	0.243 copper.
Copper that should have been found after Sieben's treatment . . . . .	0.1215
Copper found . . . . .	0.1200

#### EXPERIMENT I.

Determinations made :

1. Invert sugar separately.
2. Anhydrous dextrose separately.
3. Mixture of invert sugar and dextrose in *known* proportions.
4. Mixture of invert sugar and dextrose, after Sieben's treatment.

1. Took 13.024 gms. chemically pure sugar, dissolved in 100 cc. flask, inverted with 5 cc. HCl (German Government method).

50 cc. of the inverted solution were made up to 1000 cc. 25 cc. of this solution equal 0.1628 gms. dry substance. This was neutralized with  $\text{Na}_2\text{CO}_3$ , and the invert sugar determined by the copper test.

Result . . . . . 0.311 gram Cu.

2. 12.5 gms. anhydrous dextrose were dissolved up to 500 cc. water. 10 cc. of this solution, corresponding to 0.25 gm. dry substance, were used for the copper determination.

This determination was made three times.

Results: Determination No. 1 . . . . . = 0.473 Cu.

" " 2 . . . . . = 0.473 "

" " 3 . . . . . = 0.475 "

3. 200 cc. of solution No. 1 (= 1.3024 gms. dry substance) were mixed with 80 cc. of solution No. 2 (= 2.000 gms. dry substance). Of this mixture 35 cc. were taken for the copper determination. These 25 cc. represent, of solution No. 1, 25 cc. (= 0.1628 gm. dry substance), and, of solution No. 2, 10 cc. (= 0.2500 gm. dry substance).

Hence, if this mixture of invert sugar and dextrose should reduce copper in the *same* proportion as these sugars do separately, the amount of Cu reduced here, should be equal to the sum of the copper reduced by determination No. 1 + determination No. 2 given above, and equal to 0.784 gm. Cu. This determination was also made three times. By two minutes' boiling, there were found:

Results: Determination No. 1 . . . . . = 0.764 gram Cu.

" " 2 . . . . . = 0.769 " "

" " 3 . . . . . = 0.772 " "

Repeating this experiment once more, but boiling for *three* minutes, there was found 0.775 gm. Cu.

4. Took, of solution No. 3, 212 cc. (= 2.5 gm. dry substance.) Heated for three hours with 60 cc. six times normal strength  $\text{HCl}$ , cooled, neutralized with six times normal strength sodium hydrate, made up to 500 cc., and used 50 cc. of this solution (= 0.25 gm. dry substance) for the copper determination.

These 50 cc. consisted of:

Invert-sugar . . . . . 0.09861 grams.

Dextrose . . . . . 0.15143 "

262 DETERMINATION OF SUCROSE AND INVERT SUGAR.

0.09861 invert-sugar reduces . . . . . 0.188 Cu.  
 0.15143 dextrose reduces . . . . . 0.286 "

One-half of the invert-sugar is dextrose, hence we should *expect* a yield of :

$$\begin{array}{r} 0.188 \div 2 = 0.094 \text{ Cu} \\ 0.286 \text{ "} \\ \hline 0.380 \text{ "} \end{array}$$

and there *were* found :

$$\text{Cu} = 0.3826 \text{ grams.}$$

EXPERIMENT II

Determinations made :

1. Invert-sugar.
2. Levulose separately.
3. Mixture of invert-sugar and levulose in known proportions.
4. Mixture of invert-sugar and levulose as in No. 3, after Sieben's treatment.

1. Proceeded exactly as in No. 1 (Experiment I.) and found as there : Result = 0.311 Cu.

2. 10 cc. of a levulose solution equal 0.180 gms. dry substance reduced . . . . . 0.275 gms. Cu.

3. Used 250 cc. of solution 1. = 1.628 gms. dry substance and 100 cc. of Solution No. 2 = 1.8 gms. dry substance (of which 93.3 per cent. are levulose), or levulose = 1.6794 gms.

Of this mixture took 35 cc.; these contained : 0.1628 gms. invert-sugar (which is the dry substance of Solution No. 1), and 0.1679 gms. levulose (which is the dry substance of Solution No. 2).

These together *should* reduce copper : . . . . . 0.586

$$\begin{array}{r} \text{The 0.1628 invert sugar} = 0.311 \text{ Cu} \\ \text{The 0.1679 levulose} = 0.275 \text{ "} \\ \hline 0.586 \end{array}$$

There *were* found 0.5868 gms. Cu.

EXPERIMENT III.

Determinations made :

1. Mixture of sucrose, invert-sugar and dextrose.
2. Mixture of invert-sugar and dextrose.
3. Total dextrose in No 1, after Sieben's treatment.

Test No. 1.

	Cu Reduced.
Used : Sucrose 0.26048 grams . . . . .	0.4975 grams.
“ Invert sugar 0.013024 grams . . . . .	0.0249 “
“ Dextrose* 0.0052096 grams . . . . .	0.0095 “

Solution No. 1.—Copper reduced by :

Inverted sucrose . . . . .	0.4975
Invert sugar . . . . .	0.0249
Dextrose . . . . .	0.0095
	<hr/>
	0.5319 Cu.

Solution No. 2.—Copper reduced by :

Invert sugar . . . . .	0.0249
Dextrose . . . . .	0.0095
	<hr/>
	0.0344 Cu.

Solution No. 3.—Copper reduced by dextrose, after  
Sieben's treatment . . . . . 0.269 Cu.

Calculation.

No. 1 . . . . .	0.5319
Less No. 2 . . . . .	0.0344
	<hr/>
	$0.4975 \div 2 = 0.2487$
No. 3 . . . . .	0.2690
Less . . . . .	0.2487
	<hr/>
	$0.0203 \times 2 = 0.0406$

This value 0.0406 is greater than No. 2, hence there is free dextrose present.

No. 2 . . . . .	0.0344
Less . . . . .	0.0203
	<hr/>
	$0.0141 \times 2 = 0.0282$

No. 2 . . . . .	0.0344
Less . . . . .	0.0282
	<hr/>

0.0062 Cu due to free dextrose.

Cu due to free dextrose *placed in the solution* = 0.0095

Cu due to free dextrose, *found* . . . . . = 0.0062

Difference = 0.0033

The difference is equal to only 3.3 milligrams, but as such small quantities were worked with, the percentage of error is too great.

\*Anhydrous crystalline dextrose.



# 264 DETERMINATION OF SUCROSE AND INVERT SUGAR.

This experiment was, therefore repeated, but greater amounts of substance were used.

## Test No. 2.

	Cu Reduced.
Used : Sucrose 0.26048 . . . . .	. = 0.4975
" Invert sugar 0.026048 . . . . .	= 0.04975
" Dextrose 0.013024 . . . . .	= 0.0246

## Solution No. 1.—Cu reduced by :

Inverted sucrose . . . . .	0.4975
Invert sugar . . . . .	0.04975
Dextrose . . . . .	0.0246
	<hr/>
	0.57185 Cu.

## Solution No. 2.—Cu reduced by :

Invert sugar . . . . .	0.04975
Dextrose . . . . .	0.0246
	<hr/>
	0.07435 Cu.

Solution No. 3.—Cu reduced by dextrose after Sieben's treatment . . . . . 0.2968 Cu

## Calculation.

No. 1. . . . .	0.57185
Less No. 2 . . . . .	0.07435
	<hr/>
	0.49750 ÷ 2 = 0.2487
No. 3. . . . .	0.2968
Less . . . . .	0.2487
	<hr/>
	0.0481 × 2 = 0.0962

This value, 0.0962, is greater than No. 2, hence free dextrose is present.

No. 2. . . . .	0.07435
Less . . . . .	0.04810
	<hr/>
	0.02625 × 2 = 0.05250

No. 2 . . . . .	0.07435
Less . . . . .	0.05250
	<hr/>

0.02185 Cu due to free dextrose.

Cu due to free dextrose placed in the solution . . . . .	— 0.02460
Cu due to free dextrose found . . . . .	— 0.02185
	<hr/>
Difference . . . . .	— 0.00275

The difference is equal to 2.75 milligrams; whereas in the first test only 65.3 per cent. of the added dextrose was found, in this test 88.8 per cent. were recovered. As the differences encountered have never exceeded 3.5 milligrammes of copper, and have generally fallen below that figure, it is probable, that working with larger amounts will decrease materially the percentage of loss.

## EXPERIMENT IV.

Determinations made :

1. Mixture of sucrose invert-sugar and levulose in known proportions.
2. Mixture of invert-sugar and levulose.
3. Total dextrose in No. 1, after Sieben's treatment.

1. Used : Sucrose . . . . .	0.1628
"    Invert sugar . . . . .	0.01628
"    Levulose . . . . .	0.1898215
	<hr/>
	0.0107415

This should have reduced copper.

Inverted sucrose . . . . .	0.3110
Invert sugar . . . . .	0.0311
Levulose . . . . .	0.0088
	<hr/>
	0.3509 Cu.

There were found in Test 1, 0.3572 Cu; in Test 2, 0.3550 Cu. Calculating over to 0.25 gms dry substance *there should have been reduced* . . . . . 0.4625 copper.

There was found on 0.25 gms. dry substance :

Test 1, 0.4704 Cu.

Test 2, 0.4675 Cu.

2. Used : Invert-sugar . . . . .	0.01608
"    Levulose . . . . .	0.01007415
	<hr/>
	0.0070215

This *should* have reduced copper :

Invert sugar . . . . .	0.0311
Levulose . . . . .	0.0088
	<hr/>
	0.0399 Cu.

There were *found* Cu = 0.040.

3. Used : Same as solution No. 1. This should have reduced copper, 0.2388 (based on 0.25 gms. dry substance).

There was found by proceeding as directed by Sieben, *i. e.*, by using 60 cc. HCl of six times normal strength, and boiling for three hours 0.2934 Cu.

This proved that all the levulose was not destroyed, and indicated either more acid must be used or that the solution would have to be boiled for a longer time. Both devices were tried and both gave very satisfactory results.

*Test 1.*—Used 120 cc. HCl ( $6 \times$  normal strength). Time of boiling, three hours. Copper reduced, 0.233.

*Test 2.*—Used 60 cc. HCl ( $6 \times$  normal strength). Time of boiling, six hours. Copper reduced, 0.235.

To briefly resume, the foregoing data are here once more given in tabular form :

<i>Exp. 1.</i> —Invert sugar . . . . .	0.09861
Dextrose . . . . .	0.15143
Ratio of invert sugar to dextrose, as 100 : 154.	
Copper that should have been reduced . . . . .	0.3800
Copper found . . . . .	0.3826
<i>Exp. 2.</i> —Invert sugar . . . . .	0.1628
Levulose . . . . .	0.1679
Ratio of invert sugar to levulose, as 100 : 103.	
Copper that should have been reduced . . . . .	0.5860
Copper found . . . . .	0.5868
<i>Exp. 3.</i> —Invert sugar . . . . .	0.273504
Dextrose . . . . .	0.0052096
Ratio of invert sugar to dextrose, as 100 : 2.	
Copper that should have been reduced . . . . .	0.0095
Copper found . . . . .	0.0062
<i>Exp. 3a.</i> —Invert sugar . . . . .	0.286528
Dextrose . . . . .	0.013024
Ratio of invert sugar to dextrose, as 100 : 4.5.	
Copper that should have been reduced . . . . .	0.02460
Copper found . . . . .	0.02185
<i>Exp. 4.</i> —Invert sugar . . . . .	0.17908
Levulose . . . . .	0.0107415
Ratio of invert sugar to levulose, as 100 : 6.	
Copper that should have been reduced . . . . .	0.2388
Copper found after three hours' boiling . . . . .	0.2934
Copper found after six hours' boiling . . . . .	0.235
Copper found after three hours' boiling, with double amount of acid . . . . .	0.233

As shown by these data the proportion between the invert sugar and the dextrose, or levulose, respectively, was made to vary between wide limits.

The work thus far given shows that this method devised for the determination of sucrose, invert sugar and dextrose or levulose, respectively, is perfectly feasible and practicable.

It, however also discloses the fact that the directions given by Seiben for the destruction of the levulose—the process upon which this method of analysis depends wholly for its accuracy—do not meet *all* the possibilities. A careful investigation will therefore have to be made of the various conditions affecting the destruction of the levulose, before judgment can be passed on the value of the method here under consideration.

Experiments to this end are now in progress, and the results obtained will be given in Part II. of this paper.

For valuable aid received in the execution of the analytical work here recorded, the writer wishes to express his obligations to his assistants, Messrs. Ziebolz and Brainerd.

#### METHOD FOR THE RAPID DETERMINATION OF MANGANESE IN SLAGS, ORES, Etc.

BY FRED G. MYHLERTZ.

Weigh out  $\frac{1}{2}$  gm. of the finely powdered sample and mix it thoroughly with 5 gms. of a mixture of 3 parts sodium carbonate and 1 part potassium nitrate. Introduce the whole mass into a platinum crucible of about 30 cc. capacity, and heat gently.

The heat should be maintained at a temperature just high enough to keep the mass in a state of quiet fusion. If heated too high it has a tendency to run over.

Towards the close of the operation the mass should be heated high enough to allow it to rise in the crucible and react upon anything adhering to the sides of the crucible or lid.

After cooling, the mass is disintegrated by boiling water.

When thoroughly disintegrated, about 3 cc. of alcohol are added to reduce the sodium permanganate and precipitate all the manganese as  $MnO_2$ . Filter on an asbestos or paper filter with filter pump, and wash three times to remove any nitrites.

Transfer the precipitate back to casserole in which the fusion

was dissolved, and in which the crucible and lid are allowed to remain on account of adhering  $\text{MnO}_2$ .

Now add 100 cc. of a standard ferrous sulphate solution, stir well until completely dissolved, and, as in the well known Ford's method, titrate the excess of ferrous sulphate with bichromate solution. Calculate the amount of manganese present from the number of cc. of bichromate required.

The principal precautions to be observed are, to have a sufficiently large crucible to prevent loss by overflow, or by some of the mass escaping oxidation from being spattered on the lid.

This method requires from two to three hours, and is a vast saving of time over the usual methods. I have applied this method wholly to slags from spiegel cupolas, but doubt not that it will answer for ores as well as silicates. I find that it gives very satisfactory results.

LABORATORY ILL. STEEL CO., UNION WORKS, CHICAGO, ILL.  
May 30, 1890.

## PHOSPHORUS IN PIG-IRON, STEEL, AND IRON-ORE.\*

BY CLEMENS JONES, HOKENDAUQUA, PA.

The analytical history of phosphorus in its relation to the metallurgy of iron is an interesting study, the progress of which runs parallel with the development of the greatest industry in the world. Without the means of finding out how much phosphorus crude pig-iron contained, the Bessemer steel process would have been impossible. To do this was originally tedious and slow work. On the other hand, the "direct" process of to-day, as well as the various special processes for steel or iron, have demanded the utmost rapidity in the operations of analytical chemistry.

In general, any rapid process for the conversion of unrefined metal into a product of standard composition depends upon the rapidity of some accurate means employed to control it. Moreover, in our modern practice, it is not improbable that the differences in physical properties among the various makes of iron and steel are affected, if not produced, by the use of different methods of analysis.

Recourse is always had for correction to the "standard methods,"

\*From advance sheets Trans. A. I. M. E. sent by the author.

but I incline to think that these methods are susceptible to error. It is very certain that the system of duplicates would not be resorted to, if the fact were otherwise. Even when duplicated, under the most careful and skilful manipulations, these standard methods produce disagreements. In proof of statements like these, which may sound heretical, I hope, further on, to cite some evidence worthy of attention. I do not now mean to lay claim to the distinction of discovering the ultimate corrective. That result will come, no doubt, in time, as the product of the experience of many workers.

In the case of phosphorus, as of the other ingredients of iron or steel, a great deal has been done to accommodate the methods of analysis in vogue to the growing necessity for more rapid procedures. Much of this work has concerned what might be called the incidents of method. There is no better example of the accumulation of these incidental improvements than the work done on phosphorus; and I believe that the final successful outcome of such progressive changes will be properly considered the standard method.

The ideal analysis, both for refined conditions and delicate determinations, is to be found, in nearly all instances, in a volumetric method. But, in the preparatory stages, the treatment by this standard method must consist of *visible reactions*.

I have classified what appear to be the salient features already embodied separately in the different methods; and when so related, they apparently fulfil the conditions and the object that each has had in view.

The method of Mr. F. A. Emmerton (*Trans.*, xv., 93\*), is the real beginning of this progressive series. As recommended, certain objections were found to it. The first of these was in the use of dilute nitric acid as a wash for the yellow precipitate. Acid ammoniac nitrate, as suggested by Dr. Drown, was then substituted, with only partial success. The presence of nitric acid in the final solution, reduced for titration, seriously interfered with accurate work. I communicated this fact to Mr. A. L. Colby, chemist to the Bethlehem Iron Co., who at the time was also experimenting. His conclusion, reached by careful examination, through it

\*This Journal I, 93.

pointed out the remedy. I quote from Mr. Colby's notes, kindly placed at my disposal :

NOTES ON EMMERTON'S METHOD FOR PHOSPHORUS, OCTOBER, 1887.

*Blank Phosphorus Determination.*—A clean, dry 16-oz. Erlenmeyer flask was washed twice with am. nitrate wash ( $\text{NH}_4\text{NO}_3$ , 200 gms.;  $\text{HNO}_3$  conc., 30 cc.;  $\text{H}_2\text{O}$ , 2000 cc.), pouring it on a filter, and draining the flask as much as possible each time; the paper was then washed twice with the wash, and sucked dry; the stem of the funnel was rinsed off on the outside with water and the funnel placed in the flask; paper punctured with platinum rod, and washed with dilute  $\text{NH}_4\text{OH}$  (1 : 4), about 30 cc. being used; 5 gms. granulated zinc was added to the contents of the flask, and 80 to 90 cc.  $\text{H}_2\text{SO}_4$  of the dilution, 150  $\text{H}_2\text{SO}_4$  : 420  $\text{H}_2\text{O}$ ). A small funnel was put in the top of the flask, which was then heated till nearly all the zinc was dissolved. The reduced solution was then filtered, flask, funnel and paper were thoroughly washed with hot water, and the solution was titrated with  $\text{KMnO}_4$  at once.

A permanent tint was not obtained until 12 cc. of  $\text{KMnO}_4$  had been used. (As 1 cc. of  $\text{KMnO}_4 = .000106$  gms. P., this is equivalent to an error, in analyzing an ore where 8 gms. are taken, of 0.016 per cent., and for a steel or iron where 4 gms. are taken, of 0.032 per cent., P.).

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*Above blank test, using as a wash  $\text{HNO}_3$  (1 : 25).* Permanent tint at 8.5 cc. of  $\text{KMnO}_4$ .

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*Above blank test, using as a wash  $\text{HNO}_3$  (1 : 50, which Emmerton recommends).* Permanent tint at 3.2 cc. of  $\text{KMnO}_4$ .

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*Above blank test, using as a wash  $\text{H}_2\text{SO}_4$  (1 : 50).* Permanent tint at 0.45 cc.  $\text{KMnO}_4$ .

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*Above blank test, using as a wash  $(\text{NH}_4)_2\text{SO}_4$ , made up as follows:*  $(\text{NH}_4)_2\text{SO}_4$ , crystals, 25 gms.;  $\text{H}_2\text{SO}_4$ , conc., 50 c.c.;  $\text{H}_2\text{O}$ , 2500 c.c.  
Permanent tint at 0.45 c.c. of  $\text{KMnO}_4$ .

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Zinc 5 gms. and  $\text{H}_2\text{SO}_4$  (90 cc.), placed directly in a dry clean flask, reduced as usual, filtered, washed and titrated. Permanent tint at 0.45 c.c. of  $\text{KMnO}_4$ .

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To ascertain if yellow precipitate is soluble in  $\text{H}_2\text{SO}_4$ , or in  $(\text{NH}_4)_2\text{SO}_4$  wash, which would prevent its use as a substitute for  $\text{NH}_4\text{NO}_3$  wash. Selected crystals of  $\text{Na}_2\text{HPO}_4$ , 12  $\text{H}_2\text{O}$ , containing by theory 8.6572 per cent. P., were dissolved, 1.5408 gms. in 500 c.c. distilled water, and the following tests were made :

## TESTS WITH VARIOUS WASH-WATERS.

Date. 1887.	Test No.	Wash-Water used on yellow precipitate.	Na <sub>2</sub> HPO <sub>4</sub> solution taken c.c.	K MnO <sub>4</sub> used. c.c.	Correction for zinc.	Phosphorus per cent.
Sep. 20	1	Ammon. nitrate . . .	10	27.4	0.5	9.252
" 20	2	" " " . . .	10	26.7	0.5	9.012
" 20	3	Ammon. nitrate, and then washed twice with water to remove NH <sub>4</sub> NO <sub>3</sub> . . . . .	10	25.8	0.5	8.702
" 21	4	H <sub>2</sub> SO <sub>4</sub> (1 : 5) . . . . .	10	25.7 Zinc ran through.	0.5	8.668
" 21	5	" " " . . . . .	10	25.3	0.5	8.530
" 20	6	" (1 : 50) . . . . .	25	64.6	0.5	8.8195
" 20	7	" " " . . . . .	25	64.6	0.5	8.8195
" 21	8	" " " . . . . .	10	25.0	0.5	8.42
" 21	9	" " " . . . . .	10	24.9	0.5	8.39
" 21	10	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> . . . . .	10	25.7	0.5	8.668
" 21	11	" " " . . . . .	10	25.7	0.5	8.668

As the blanks run both with H<sub>2</sub>SO<sub>4</sub> wash (1 : 50) and with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> wash used up 0.45 c.c. KMnO<sub>4</sub> instead of 0.5 c.c., as subtracted above, analyses Nos. 4, 10 and 11 should show 8.685 per cent. instead of 8.668 P.

The above analyses, using 10 c.c., were made on too small a quantity of Na<sub>2</sub>HPO<sub>4</sub>. Small variations in KMnO<sub>4</sub> make too large differences in per cent. of P., 0.5 c.c., or one drop of KMnO<sub>4</sub>, being equal to .007 per cent. P.

But the set of analyses shows that even strong H<sub>2</sub>SO<sub>4</sub> (1 : 5) exercises no appreciable solvent action on yellow precipitate, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> wash is rather better in agreement than H<sub>2</sub>SO<sub>4</sub> (1 : 50).

As an example of the possibilities of the method when using the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> wash for determination of small amounts of P., a solution of C. P. Fe<sub>2</sub>Cl<sub>6</sub> was tested. Of this solution, which had been prepared from the filtrate from P. determinations in pig-iron, by precipitation with NH<sub>4</sub>OH, thorough washing, and solution in HCl, 25 c.c., containing about 2.5 gms. Fe, were precipitated for P. as usual; the cloud of yellow precipitate was filtered off, washed with H<sub>2</sub>SO<sub>4</sub> (1 : 50), dissolved, reduced, etc., as usual, titration giving only 0.75 c.c. KMnO<sub>4</sub>, which, after zinc correction of 0.5 c.c. equalled 0.001 per cent. phosphorus—a result not obtainable when using NH<sub>4</sub>NO<sub>3</sub> wash.

In addition, the following tests of ores were made, using (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> wash for the volumetric determinations, and washing four times on the paper (instead of twice, to test the solvent action, if any) and twice in flask.

Sept. 23—*Filtration by suction*, taking the usual precaution of draining flasks and funnels, and washing stem of funnel.

10 gms. of ore dissolved;  $\frac{80}{100}$  taken for phosphorus.



		P. per cent.	
No. 1524, . . . . .	20.9 c.c. $\text{KMnO}_4$	=0.027.	} After deducting 0.5 c.c., cor- rection for Zn.
" 1525, . . . . .	14.8 c.c. "	=0.020.	
" 1526, . . . . .	7.6 c.c. "	=0.010.	

Sept. 28.—*Gravimetric determination* on 10 gms. ore,  $\frac{80}{100}$  taken for phosphorus, using  $\text{NH}_4\text{NO}_3$  wash, twice in funnel, and twice in flask—other conditions as before, but making two precipitations of  $\text{NH}_4\text{MgPO}_4$  before weighing as  $\text{Mg}_2\text{P}_2\text{O}_7$ .

	$\text{Mg}_2\text{P}_2\text{O}_7$ Gms.	P. per cent..
No. 1524, . . . . .	0.0079	= 0.025
" 1525, . . . . .	0.0062	= 0.022
" 1526, . . . . .	0.0026	= 0.009

Mr. Colby's notes close with some additional tests which confirm the foregoing.

Concerning the use of acid ammonic sulphate, it is interesting to note that, nearly a year later, Mr. Porter W. Shimer, in a paper before the Institute (*Trans.*, xvii., 100)\*, observes: "Sulphuric acid and *ammonium sulphate* completely take the place of nitric acid and ammonium nitrate."

In the same paper Mr. Shimer describes the use of potassium permanganate as an oxidizing agent. This appears to be the next important detail. By means of it the complete oxidation of the phosphorous to ortho-phosphoric acid, as Dr. Drown puts it, is accomplished. This is indispensable, and cannot be omitted in the solution of pig-iron, steel or iron-ore.

Dr. Drown's method (*Trans.*, xviii.)† of dissolving pig-iron or steel in nitric acid of 1.135 specific gravity, in which potassium permanganate, as suggested by Mr. Shimer, is used as an oxidizing agent, is a most happy expedient. It opens the way to the most rapid method in use. There is no ground to doubt its efficacy, if applied to iron-ore, by taking advantage of a simple device, namely, solution in dilute sulphuric acid of the fused residue from the ore. According to Dr. Drown, silicon exerts no influence on the determination of phosphorus in pig-iron or steel. As a *soluble silicate* there is good evidence of its non-interference in the treatment of iron-ore. A determination in iron-ore can thus be made in nearly the same time as in iron or steel.

\*This Journal 2, 283.

†This Journal 3, 288.

Here, then, seem to be collected nearly all of the requisite conditions. There is but one remaining, the reduction of the molybdic acid. I believe that this is fully covered by using the method discovered by me for reducing ferric solutions (*Trans.*, xvii., 411)\*. I have found that it applies in all respects equally well to the complete and instantaneous reduction of molybdic acid.

It is possible then to reconstruct a method, based on these incidents, which should be peculiarly adapted to every demand for the rapid and accurate determination of phosphorus.

Before advancing so far, however, I propose to show with what degree of accuracy these principles may be employed, by giving the following results. There were obtained by the Emmerton method, modified by the use of ammoniac sulphate in washing the yellow precipitate, and by the use of the reductor.

*No. 3588.—Pig-Iron.*

<i>Weight.</i> <i>gm.</i>	<i>KMnO<sub>4</sub>.</i> <i>c.c.</i>	<i>Correction</i> <i>c.c.</i>	<i>Phosphorus.</i> <i>per cent.</i>
.5000	18.67	0.03	0.447
.5000	18.52	0.03	0.443

1 c.c.  $\text{KMnO}_4 = 0.00012 \text{ P.}$

*No. 3980.*

	<i>Phosphorus.</i> <i>per cent.</i>
No. 1, gravimetric, . . . . .	0.717
No. 2, volumetric, . . . . .	0.720

The following comparison is between this method (called "Reductor") applied to iron-ore, and the Emmerton method of adding the zinc directly.

*No. 4260.*

	<i>Weight Taken.</i> <i>gms.</i>		<i>KMnO<sub>4</sub>.</i> <i>c.c.</i>	<i>Phosphorus.</i> <i>per cent.</i>
A, . . . . .	1.9700	Emmerton,	16.9 —0.2	0.101
B, . . . . .	2.6078	"	20. —0.2	0.091
C, . . . . .	2.8800	Reductor,	22.15—0.05	0.092
D, . . . . .	3.0760	"	23.81—0.05	0.092

*No. 4261.*

	<i>Weight taken.</i> <i>gms.</i>		<i>KMnO<sub>4</sub>.</i> <i>c.c.</i>	<i>Phosphorus.</i> <i>per cent.</i>
A, . . . . .	1.6901	Emmerton,	30.01—0.2	0.212
B, . . . . .	1.9439	"	34.5 —0.2	0.211
C, . . . . .	1.9915	Reductor,	36.9 —0.05	0.222
D, . . . . .	1.9982	"	37.1 —0.05	0.222

\*This Journal 3, 123.

In the series following, carried through like the foregoing, potassium permanganate was used to oxidize the solutions. This was done carefully, before adding the ammonia. The improvement is marked.

*No. 3681.—Pig-Iron.*

<i>Weight.</i> <i>gms.</i>	<i>KMnO<sub>4</sub>.</i> <i>c.c.</i>	<i>Correction.</i> <i>c.c.</i>	<i>Phosphorus.</i> <i>per cent.</i>
.5025	2.83	0.05	0.066
.5030	2.72	0.05	0.063

Determination by Mr. Shimer, by his Mb-Mg method, . . . 0.064

The small amount of the sample necessitated the low weights, which, in that measure, affected the determination.

*No. 3680.—Pig-Iron.*

<i>Weight.</i> <i>gms.</i>	<i>KMnO<sub>4</sub>.</i> <i>c.c.</i>	<i>Correction.</i> <i>c.c.</i>	<i>Phosphorus.</i> <i>per cent.</i>
.5000	26.39	0.05	0.6321
.5000	26.4	0.05	0.6324

Determination by Mr. Shimer, by his Mb-Mg method, . . . 0.615

*No. 3682.—Pig-Iron.*

<i>Weight.</i> <i>gms.</i>	<i>KMnO<sub>4</sub>.</i> <i>c.c.</i>	<i>Correction.</i> <i>c.c.</i>	<i>Phosphorus.</i> <i>per cent.</i>
.2500	23.21	0.05	1.111
.2500	23.21	0.05	1.111

Determination by Mr. Shimer, by his "sulphuric-acid" method, 1.07

The conclusion to be drawn, is not that the direct use of zinc always gives uniformly low results (by reason of the higher correction), but that the same errors are introduced, as I have pointed out in the case of the reduction of ferric solutions.

Mr. Emmerton remarks that the "port-wine" color is evidence of only incipient oxidation. On the contrary, this oxidation is very appreciable. It is only otherwise (*i.e.*, the molybdous acid oxidizes slowly), as shown by Wernecke, when completely reduced.

The color of these solutions, as ordinarily diluted, is always olive-green. By using the reductor, this color is invariably obtained. The following result, from a piece of iron, shows that it is applicable to very high-phosphorus iron ;

<i>Weight.</i> <i>gms.</i>	<i>KMnO<sub>4</sub>.</i> <i>c.c.</i>	<i>Correction.</i> <i>c.c.</i>	<i>Phosphorus.</i> <i>per cent.</i>
.5033	177.35	0.05	4.227

The color of this solution was almost opaque until diluted. It was reduced instantly.

Dr. Drown's method, I have found capable of being modified to great advantage. A large number of trials were made, in strict accordance with the method as described, but neither the organic salts nor the acids gave acceptable results. Suspecting the trouble to lie in the use of these, I substituted ferrous sulphate, which has the advantage of dissolving the manganic oxide immediately, and being simultaneously oxidized. But the drawback to its use was that a correction for phosphorus had to be applied. None of the samples of ferrous sulphate received from a number of sources as "strictly C. P." were even low in phosphorus.

Messrs. Baker and Adamson, of Easton, Pa., kindly offered to experiment, and have succeeded in making the salt free from phosphorus. This was used in all of the determinations following.

The temperature of 90° C. was also found to be too high, molybdic acid precipitating in consequence. By adhering to 85° C., as recommended by Mr. Emmerton, this was overcome. Certain irons, high in manganese or fine graphite, cannot be easily oxidized before filtration. It is advisable always to test the solution with a few drops of  $\text{KMnO}_4$ , before adding the molybdate solution.

The method for pig-iron and steel now stands as follows :

Dissolve in nitric acid of 1.135 specific gravity, according to Dr. Drown ; allow the solution to boil one minute, then add the solution of potassium permanganate ; after  $\text{MnO}_2$  appears, add a few small crystals of ferrous sulphate. Filter solution into flask. Add sufficient  $\text{NH}_4\text{OH}$  (.90 specific gravity); when solution clears up, add a few drops of  $\text{KMnO}_4$ , to insure oxidation, again dissolving, if necessary. At 85° C. add to the solution 75 cc. ammonic molybdate solution (Dr. Drown's formula), and agitate violently for five minutes. Filter in Bunsen filter-flask, and wash thoroughly with ammonic sulphate, observing all the precautions indicated by Mr. Colby. Dissolve the yellow phospho-molybdate in ammonia (96 specific gravity), *without* puncturing paper. Wash once or twice with water. Suck dry, and remove flask and stopper to suitable bell-glass. Pour the ammonia solution into small beaker, washing out flask with water three times. Place this flask under the

bell-jar and again filter the ammonia solution into it, this time washing paper thoroughly with water. Wash the zinc in the reductor, as required for ferric solutions. Then add 30 cc. to 50 cc. sulphuric acid (1.32 specific gravity) to the ammoniacal solution, and filter through the reductor by strong suction, washing the same as indicated for ferric solutions, and titrate as usual. The correction for zinc is obtained as described. I have made determinations in this way in half an hour. The following results were obtained, in the above manner :

The first is a "standard steel" which has been repeatedly tried by various chemists. The phosphorus is considered to be between 0.064 and 0.065. Below is a table, giving the former results, and the methods employed, the chemist being indicated by letters :

*No. 4768.—Standard Steel.*

<i>Chemist.</i>	<i>Phosphorus. per cent.</i>	<i>Method.</i>
A, . . . . .	0.063	Emmerton.
" . . . . .	0.064	"
" . . . . .	0.065	"
B, . . . . .	0.063	"
" . . . . .	0.065	"
C, . . . . .	0.063	Not given.
" . . . . .	0.065	" "
" . . . . .	0.065	" "
D, . . . . .	0.0603	" "
E, . . . . .	0.061	Weighs yellow ppt.
F, . . . . .	0.0666	Magnesia method.
" . . . . .	0.0650	" "
" . . . . .	0.0651	Weigh yellow ppt. original.
G, . . . . .	0.0660	" " " "
H, . . . . .	0.061	Magnesia method.
" . . . . .	0.065	Titration of solution from the same $\text{NH}_4\text{MgPO}_4$ .

This steel yielded, by the method I have above described, the following results :

<i>Weight taken. gms.</i>	<i>KMnO<sub>4</sub>. c.c.</i>	<i>Correction. c.c.</i>	<i>Phosphorus. per cent.</i>
3.1264	16.89	0.05	0.0646
3.1267	16.86	0.05	0.0645

The following determination was made in fifty minutes from the start :

<i>Weight taken.</i> <i>gms.</i>	<i>KMnO<sub>4</sub>.</i> <i>c.c.</i>	<i>Correction.</i> <i>c.c.</i>	<i>Phosphorus.</i> <i>per cent.</i>
3.5014	18.52	0.05	0.0633

Value of 1 c.c.  $\text{KMnO}_4$ , 0.00012 gms. phosphorus.

A sample of Swedish pig-iron was tried in like manner. The former determinations were :

*No. 5009.*

<i>Method.</i>	<i>Phosphorus.</i> <i>per cent.</i>
Emmerton, . . . . .	0.023
" . . . . .	0.023
" . . . . .	0.023
" . . . . .	0.023
Magnesia Gravimetric, . . . . .	0.023
" . . . . .	0.022

This gave the following by my method :

<i>Weight.</i> <i>gms.</i>	<i>KMnO<sub>4</sub>.</i> <i>c.c.</i>	<i>Correction.</i> <i>c.c.</i>	<i>Phosphorus.</i> <i>per cent.</i>
3.5187	6.87	0.05	0.0232

A second determination, completed in fifty minutes,  $P = 0.024$ .

The method was also applied to iron-ore. This was dissolved in hydrochloric acid (1.12 sp. gr.) and filtered. The filtrate was evaporated with nitric acid in the usual way. The residue was fused with excess of sodium carbonate, and then dissolved in the original beaker in dilute sulphuric acid and water. This solution was added to nitric acid solution, which was transferred to a flask, oxidized with potassium permanganate, and then treated like the iron solution.

*No. 4995.—Rubio Ore.*

<i>Former Determination.</i>	<i>Phosphorus.</i> <i>per cent.</i>
Emmerton Method, residue not fused, . . . . .	0.012
" " " fused, . . . . .	0.011
I. By method described above, . . . . .	0.013
II. In way described for results Nos. 4260-61, this ore gave . . . . .	0.0118

Another Bessemer ore, of which the former determinations were as follows :

*No. 5008.*

	<i>Phosphorus.</i> <i>per cent.</i>
Emmerton method, not fused, . . . . .	0.016
" " . . . . .	0.016
" " . . . . .	0.016

Gave the results by the methods referred to in No. 4995, I.  
and II.:

I. Method, . . . . .	0.017
II. " . . . . .	0.018

There is no loss of time in fusing the residue by this plan, and it is a desirable precaution under any circumstances.

In pig-iron or steel, arsenic and titanium interfere with the accuracy of the rapid method. The former must always be separated, and retards the process materially. In fact, the presence of arsenic may be regarded as an obstacle to the determination of phosphorus by any method.

Titanium, probably as titanomolybdate, has an apparent influence on the determination of phosphorus by the rapid method. When the Emmerton method of evaporating the original solution to hard dryness is used, this influence is lessened, but if titanium be present in any appreciable amount, the results are vitiated. The following case by each method is a good example:

*No. 4706.—Pig-Iron (containing Titanium).*

	<i>Phosphorus. per cent.</i>
By Mr. Shimer, Mb-Mg method, . . . . .	0.659
By the Emmerton method, modified as in 3680-81-82, . . . .	0.649
" " " " . . . . .	0.643
" " " " . . . . .	0.654
" " " " . . . . .	0.650
" " " " . . . . .	0.647
" Rapid method, . . . . .	0.726
" " " " . . . . .	0.719

It may not be amiss to refer to the importance of a freshly prepared solution of the molybdic acid, which should stand twenty-four hours, at least, before use. Dr. Drown's formula (*Trans.*, xviii.), has given the best result after several years' trial. The solution must be filtered through asbestos as required.

A summary of the procedure may be found convenient:

*Rapid Method for Pig-Iron or Steel.*

- I. Dissolve in 60 c.c. nitric acid (sp. gr. 1.135.)
- II. Boil one minute (after action ceases.)
- III. Add 5 c.c. potassium permanganate (or until  $\text{MnO}_2$  precipitates).
- IV. Dissolve the  $\text{MnO}_2$  with ferrous sulphate\* (a few grains usually).

\* This may be obtained of Baker & Adamson, Easton, Pa., free from phosphorus.

- V. Filter into flask (500 cc. capacity).
- VI. Add 10 c.c.  $\text{NH}_4\text{OH}$  (sp. gr. 0.90).
- VII. Test for oxidation (III. and IV.) This is done while solution is heating.
- VIII. Add 75 c.c. molybdate solution at  $85^\circ \text{C.}$ , and shake vigorously for five minutes.
- IX. Filter and wash with ammoniac sulphate.
- X. Dissolve in  $\text{NH}_4\text{OH}$  (sp. gr. 0.96). Observe precautions.
- XI. Add 30 to 50 c.c. sulphuric acid (1 : 2 water) and filter through reductor, observing precautions mentioned (*Trans.*, xvii., 414).
- XII. Titrate.

*Rapid Method for Iron-Ores.*

- I. Dissolve in hydrochloric acid (1.12 sp. gr).
- II. Filter. Evaporate filtrate with nitric acid (1.20 sp. gr).
- III. Fuse residue with excess of sodium carbonate, and dissolve in dilute sulphuric acid (1 : 2 of water). Combine solutions when the filtrate with nitric acid is ready. Then proceed as above, from III. to end.

An accurate determination of phosphorus in pig-iron or steel, in cases uncomplicated by arsenic or titanium, can thus be made in less than an hour. For iron-ore but little more time will be necessary.

The three vital conditions of the volumetric method, solution, oxidation and reductions, by visible reactions, give the method great advantage over any other. From the number of trials made with it, the conclusions seems unavoidable, that, compared with the "magnesia" method, the results are quite as accurate, and certainly more closely accordant. The principles are correct, and I believe that the method can be demonstrated to possess all the requisites for filling the difficult role of a standard method.

I wish to acknowledge my indebtedness to Dr. Drown, Mr. A. L. Colby and Mr. Porter Shimer for samples and valuable information.

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NOTE ON THE RELATIVE EFFICIENCY OF THE  
SOLVENTS USED IN THE EXTRACTION OF  
FAT FROM MILK SOLIDS.

BY H. DROOP RICHMOND.

In a recent discussion between Dr. Davenport and myself, we disagreed as to the relative suitability of ether and petroleum ether as solvents for milk fat, and in order to settle the question I un-



dertook a series of comparative estimations ; from various causes I am now precluded for some months from continuing this investigation, but having obtained a few results they seem to be of sufficient interest for publication.

My determinations are limited to seven experiments with Adams' coils (previously extracted with acid alcohol and giving no residue to ether) the solvents used being ether, petroleum ether and chloroform ; the method used was this : 5 cc. of milk was pipetted on to a coil suspended from the edge of a table, and this was allowed to air dry ; the coil was then rolled up and extracted in a Soxhlet's apparatus for 3 hours, the solvent evaporated and the fat dried at 100° C. ; 5 cc. of alcohol was added to the flask containing the fat, gently warmed, and the acidity titrated with  $\frac{n}{20}$  alkali, phenol-phthalein being used as indicator ; the amount of alkali used minus that required to produce a red color with the alcohol and phenol-phthalein alone (usually two drops) was calculated into percentages of Lactic Acid ; the coils were then extracted for another 6 hours.

The mean of the results obtained were :

	<i>Fat estimated in 3 hrs.</i>	<i>Fat estimated in 6 hrs. more.</i>	<i>Total Fat.</i>	<i>Acidity as Lactic Acid.</i>
Ether . . . . .	3.42	.04	3.46	.062
Petroleum Ether . . . . .	3.28	.14	3.42	.054
Chloroform . . . . .	3.385	.07	3.455	.060

These results show that ether extracts the fat more readily than chloroform and still more so than petroleum ether ; I attribute this to the fact that the coils being only air-dried still contained some water, and ether having greater solvent powers for water than chloroform and still more than petroleum ether, would in this case reach the fat more readily than either of the other two solvents ; the amounts of total fat and of acidity are sensibly the same, and show that all three solvents if the extraction is carried on long enough give practically the same results, and no one solvent has in this respect any real advantage of the others ; ether however, is to my mind the most convenient as it extracts the fat from the coils faster than the other solvents, chloroform coming next ; chloroform was included in this investigation, as during several months of the year the temperature of the laboratory here approaches the boiling point of ether, and, consequently, the use of the latter solvent presents difficulties.

I had intended to continue this investigation to determine whether, on completely drying the milk residues, there is any practical difference between the solvents, and also whether the acidity is actually due to lactic acid or not; with respect to this last point the following theoretical assumption sheds some light on the subject; the results above show about 2% of lactic acid in the milk fat; this would raise the density from .93 (Fleischmann *Landw. xxxiii*, 251,) to .936, a figure approaching that which I have calculated for the density of fat in milk, .939 (*Analyst*, XIV, 121,) this figure was deduced from the analysis of milk at least one day old; I have also had the opportunity of examining two series of analyses made at dairies for the purpose of milk control and much fresher than my own and calculate the density of milk-fat at .930 and .932 respectively, figures approaching that of Fleischmann; thus it would seem that the fat is the solvent for the lactic acid produced by fermentation in milk by the time it reaches the analyst; this point, however, requires considerably more investigation before we can pronounce an authoritative opinion on the subject.

In conclusion, my experiments, though few in number, do not give any indication of the marked superiority claimed for petroleum ether on theoretical grounds, but they are too limited to enable me to draw an absolute conclusion; I regret that I can not longer now continue this investigation, and should no other chemist take up this subject, I propose to return to it when I am again at liberty.

KHEDIVIAL LABORATORY, CAIRO.

## FLUORITE FROM YORK, PA.

BY C. H. EHRENFELD.

Occurs associated with small rhombohedra of calcite in veins of massive calcite in the blue limestone. It is crystalline in structure, though no perfect crystals have been observed. It varies in color from light to dark purple. Sp. gr.=3.13. Analysis showed the usual composition, the Fl being determined by difference.

$$\begin{array}{r} \text{Ca} = 48.76\% \\ \text{Fl} = 51.24\% \\ \hline 100.00\% \end{array}$$

COLLEGIATE INSTITUTE, YORK, PA.  
May 10, 1890.

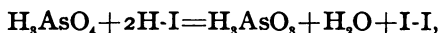
## A METHOD FOR THE REDUCTION OF ARSENIC ACID IN ANALYSIS.\*

BY F. A. GOOCH AND P. E. BROWNING.

[Contributions from the Kent Chemical Laboratory of Yale College.—III.]

Holthoff's development of Mohr's suggestion relative to the reduction of arsenic acid to the lower condition of oxidation by the action of sulphurous acid,† with the demonstration that arsenic acid can be evaporated even to dryness in presence of hydrochloric acid without danger of significant volatilization, has placed the analysis of ordinary compounds of arsenic, both natural and artificial, within the scope of Mohr's classical and exact method of determination by titration with iodine. As Holthoff left the method, it is satisfactory so far as regards accuracy, and as modified by McCay,‡ who substitutes for the four hours' digestion heating for one hour in a pressure-bottle, is eminently successful. In the account of the experiments about to be described we detail our experience in an attempt to shorten still further the process of reduction of arsenic acid by making use of hydriodic acid as the active agent instead of sulphurous acid.

In a recent paper§ we have described a method for the determination of iodine in haloid salts based upon the action of arsenic acid, in the presence of sulphuric acid, according to the equation,



the iodine being completely volatilized, but leaving behind in the arsenious acid produced by the action the record of the amount of hydriodic acid originally present. This reaction we propose to utilize conversely, and to employ potassium iodide in excess, in presence of sulphuric acid, to bring about the reduction of the arsenic acid to arsenious acid which may be determined, after neutralization, by the iodine method. The conditions of the methods are different in that, in the former the hydriodic acid is entirely broken up by the action of the arsenic acid, and the iodine volatilizes easily; while in the latter some hydriodic acid must remain in solution until a very low degree of concentration

\* Am. J. Sci., July, 1890.

† Zeit. f. anal. Chem., vol. xxiii, p. 378.

‡ Am. Chem. Jour., vol. vii, p. 373.

§ Am. J. Sci., vol. xxxix, p. 188. See this Journal, p. 124.

is reached, and remaining must exhibit its characteristic proneness to retain free iodine.

We find in practice that when a solution made up to contain sulphuric acid, an arseniate and potassium iodide to an amount somewhat in excess of that theoretically demanded to effect the conversion of the arsenic acid to arsenious acid, is boiled, iodine is evolved and the color of the liquid passes from the dark red when the iodine is abundant through the various gradations of tint to a canary yellow, and then, as the sulphuric acid reaches a degree of concentration sufficient to determine by its own specific action the liberation of iodine, the color again darkens, and if the process of concentration is continued, and much arsenic is present, crystals of arsenious iodide separate and form more abundantly on cooling. If evaporation is pushed still farther the arsenious iodide begins to volatilize and at the point where the sulphuric acid fumes the liquid loses all color and the arsenic has vanished more or less completely. In one experiment conducted in this manner it was found, by the method to be described later, that of 0.3861 grm. of arsenic pentoxide originally present with 1 grm. of potassium iodide and 10 cm<sup>3</sup> of sulphuric acid [1 : 1] the equivalent of 0.1524 grm. remained. In another similar experiment in which, however, only a few milligrams of arsenic oxide were involved not a trace of arsenic remained at the end.

It is obvious that two points in this course of action demand examination at the outset. First, means must be found for removing the remnant of free iodine which is withheld by the hydriodic acid; or of rendering it harmless in the titration process to follow; and, secondly, the degree to which the solution may be concentrated without loss of arsenic must be fixed. In our work upon the converse of this process, we noted particularly the marked influence of the amount of sulphuric acid present upon the degree of concentrating necessary to expel the iodine. We turned attention, therefore, at once to this point in the present case and investigated the effect of varying the proportion of sulphuric acid in solutions containing definite amounts of potassium iodide and potassium arseniate. The volume of the solution was made up to about 100 cm<sup>3</sup> and concentrated by boiling until the color was faintest. Then, to determine provisionally, and for pre-

liminary purposes, the point at which volatilization of arsenic was likely to occur, the concentration was continued until the arsenious iodide began to separate. The results are tabulated as follows :

KI.	As <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub> [1:1]	Volume when color was lightest.	Volume when AsI <sub>3</sub> appeared.
1 gm.	0.1900 gm.	20 cm. <sup>3</sup>	80 cm. <sup>3</sup>	33 cm. <sup>3</sup>
1 "	0.1900 "	15 "	65 "	25 "
1 "	0.1900 "	10 "	40 "	19 "
1 "	0.1900 "	5 "	30 "	11 "

The amount of sulphuric acid which, considering rapidity in concentrating to the proper point, ease in neutralizing the acid previous to titration, and general convenience in manipulation, seemed to be best, was 10 cm.<sup>3</sup> of the mixture made by diluting the acid with an equal volume of water. This we fixed upon for use in future experiments, and set the limit of concentration at 40 cm.<sup>3</sup>.

It is manifest from the phenomena described that when much hydriodic acid remains in the solution the last portions of free iodine cannot be completely removed by heat without volatilization of the arsenic. We experimented, therefore, upon the effect of very dilute sulphurous acid upon the remnant of iodine in liquids constituted as described, and concentrated to 40 cm.<sup>3</sup>, the point of minimum color, the solution of sulphurous acid which we employed corresponding approximately to centinormal iodine. We found that upon adding the sulphurous acid drop by drop to the hot concentrated solution, the point at which the color vanished could be determined without difficulty, but that if the solution was permitted to stand a single minute, the color of iodine returned, doubtless developed by the action of air upon the hot hydriodic acid. We adopted, therefore, the plan of at once diluting the solution with cold water as soon as the sulphurous acid had done its work, and immediately neutralizing with potassium carbonate. When this mode of proceeding was followed, we were unable to find evidence of reversion of arsenious acid to arsenic acid, magnesia mixture producing in the solution no precipitate of the ammonium magnesium arseniate.

Following out the same general lines, therefore, we proceeded to the quantitative examination of the process. Portions of a

standard solution of the dihydrogen potassium arseniate were measured from a burette into counterpoised Erlenmeyer flasks of 250 cm.<sup>3</sup> capacity, and the increase in weight was taken as the measure of the actual amount of the solution employed. Potassium iodide in solution, and 10 cm.<sup>3</sup> of sulphuric acid [1:1] were added, and the liquid was diluted with water to a volume of about 100 cm.<sup>3</sup>. A trap made, as described in our paper upon the reverse of this process, by cutting down a two-bulbed drying tube, was hung in the neck of the flask to prevent mechanical loss, and the liquid was rapidly concentrated by boiling until the volume of 40 cm.<sup>3</sup>, the point at which the color of iodine had faded to a pale yellow, was reached. At this point the flask was removed from the flame, its sides and the trap were quickly washed down, the weak sulphurous acid was added drop by drop from a burette until the color of the free iodine had just vanished, the liquid was immediately diluted with cold water, the free acid was nearly neutralized with potassium carbonate, and the point of neutralization was reached and passed a little by the addition of the acid potassium carbonate. After cooling completely, a definite amount of starch solution was added and the titration of the arsenious acid was proceeded with as usual, due correction being made for the amount of iodine necessary to produce the end color into the volume of liquid and starch solution employed.

The value of the standard solution of the arseniate was fixed by two series of determinations. One series was made according to Levöl's method of precipitating the ammonium magnesium arseniate and weighing as the pyroarsenate, modified, however, in that the precipitate was collected on asbestos in a perforated crucible, and ignited after moistening with ammonium nitrate. In the second series, McCay's modification\* of Reich's method was followed, excepting that the silver arseniate was collected, dried and weighed on asbestos in a perforated crucible. The mean of several closely agreeing determinations gave for the contents of 50 gms. of the solution in arsenic pentoxide as 0.3824 gm. by Levöl's method and 0.3830 gm. by McCay's modification of Reich's process. We took the mean of these figures 0.3827 gm. as the standard of the solution.

\*Am. Chem. Jour., vol. viii, p. 77.

The details of the experiments with this solution are recorded in the following table :

KI taken.	H <sub>2</sub> SO <sub>4</sub> [1:1] taken.	As <sub>2</sub> O <sub>5</sub> taken.	As <sub>2</sub> O <sub>5</sub> found.	Error.
1.5 gm.	10 cm. <sup>8</sup>	0.3861 gm.	0.3862 gm.	0.0001 gm. +
1.5 "	10 "	0.3862 "	0.3856 "	0.0006 " —
1.5 "	10 "	0.3861 "	0.3862 "	0.0001 " +
1.5 "	10 "	0.3860 "	0.3862 "	0.0002 " +
1.5 "	10 "	0.3863 "	0.3862 "	0.0001 " —
1.5 "	10 "	0.3862 "	0.3862 "	0.0000 " —
1 "	10 "	0.1927 "	0.1922 "	0.0005 " —
1 "	10 "	0.1928 "	0.1922 "	0.0006 " —
1 "	10 "	0.1930 "	0.1925 "	0.0005 " —
1 "	10 "	0.1930 "	0.1927 "	0.0003 " —
1 "	10 "	0.1936 "	0.1929 "	0.0007 " —
1 "	10 "	0.1929 "	0.1928 "	0.0001 " —

Experiments in which smaller quantities of arsenic were handled were made similarly, excepting that the standard solution, from which portions for the tests were measured, was made by diluting the former standard ten times, and centi-normal iodine was used in the titration.

KI taken.	H <sub>2</sub> SO <sub>4</sub> [1:1] taken.	As <sub>2</sub> O <sub>5</sub> taken.	As <sub>2</sub> O <sub>5</sub> found.	Error.
1 gm.	10 cm. <sup>8</sup>	0.0383 gm.	0.0380 gm.	0.0003 gm. —
1 "	10 "	0.0383 "	0.0385 "	0.0002 " +
0.5 "	10 "	0.0383 "	0.0384 "	0.0001 " +
0.4 "	10 "	0.0383 "	0.0385 "	0.0002 " +
0.3 "	10 "	0.0383 "	0.0386 "	0.0003 " +
0.2 "	10 "	0.0383 "	0.0384 "	0.0001 " +
0.2 "	10 "	0.0076 "	0.0074 "	0.0002 " —
0.2 "	10 "	0.0076 "	0.0074 "	0.0002 " —
0.2 "	10 "	0.0038 "	0.0034 "	0.0004 " —
0.2 "	10 "	0.0038 "	0.0034 "	0.0004 " —

When the amount of hydriodic acid in solution is small, correspondingly small amounts of iodine are retained after concentration. In the following experiments, colorless solutions were obtained, and, for the sake of comparison with the previous results, these solutions were neutralized and titrated without treatment with sulphurous acid, there being no apparent need for adding it in these cases.

KI taken.	H <sub>2</sub> SO <sub>4</sub> [1:1] taken.	As <sub>2</sub> O <sub>5</sub> taken.	As <sub>2</sub> O <sub>5</sub> found.	Error.
0.2 gm.	10 cm. <sup>3</sup>	0.0038 gm.	0.0035 gm.	0.0003 gm. —
0.2 "	10 "	0.0038 "	0.0035 "	0.0003 " —

It appears, therefore, that the average error of the whole number of determinations (24) made by this process amounts to rather less than 0.0002 gm. —, falling between extremes of 0.0003 gm. + and 0.0007 gm. —. The entire amount of arsenic pentoxide handled in the twenty-four determinations was 3.7352 gms., and of this 3.7309 gms. were indicated in the titration as reduced to the arsenious condition. The loss 0.0047 gm.—the entire error of the process—amounts to 0.13 per cent. of the amount taken.

Certain experiments were made to see whether the period of evaporation might not be dispensed with by so modifying the process that the entire amount of iodine set free in the action of the sulphuric acid, the arseniate, and the iodide might be reconverted at once by sulphurous acid to the condition of hydriodic acid. The conversion was apparently successful, but the results of the modification were several per cent. below the truth, indicating that the digestion during evaporation, or the removal of the free iodine, or the combined effect of the two, is essential to the completion of the reduction of the arsenic.

The process as we recommend it may be summarized briefly, as follows: To the arseniate in solution are to be added potassium iodide in excess of the amount needed according to the equation, to complete the reduction, and 10 cm.<sup>3</sup> of half and half sulphuric acid. The liquid is to be diluted to about 100 cm.<sup>3</sup> and boiled rapidly (with the precautions of trapping as described) until the volume is decreased to 40 cm.<sup>3</sup>. The color of free iodine is to be bleached by cautious additions of sulphurous acid (corresponding roughly to centinormal iodine) and instantly diluted with water and neutralized with potassium carbonate, the neutral carbonate at the first, and afterward the acid carbonate. The whole is to be cooled and titrated as usual with iodine, using starch as an indicator. Its advantage is in the rapidity with which it may be executed, the whole operation being easily completed in a half-hour.



# DETECTION AND QUANTITATIVE ESTIMATION OF INORGANIC AND ORGANIC POISONS IN BODIES.

BY DR. ANTON SEYDA.\*

## INTRODUCTION.

Although toxicologists have at their disposal a vast amount of chemical literature, I hope this article will be welcome to many, particularly as it is the result of my own experience and observations. My object has been to find a practical qualitative and quantitative course for the detection of those poisons which are within reach of the public, without troubling about such bodies as bitters, drastics, etc., which, in the present state of science, cannot be detected with certainty, whatever care and material the analyst might waste on the matter.

The analysis consists of a preliminary examination, and the regular chemical course. The expert conducting such an investigation must never omit to make the fullest inquiries about the case, as often valuable clues will be obtained, saving an immense deal of time and trouble.

## PRELIMINARY TESTS.

### (a) *Blood.*

The blood is often in a state of partial decomposition, particularly if a long time has elapsed between the time of death and the investigation. The reduction of its coloring-matter is more or less complete, so that a spectroscopical examination is, of course, useless. If the blood should be dry, it may be dissolved by water containing a trace of caustic soda. The spectrum of a partially reduced blood mostly shows a continued broad absorption band, which is composed of three lines, viz., two of oxyhæmoglobin, with the hæmoglobin one between. Sometimes the band is accompanied by another line in the red part of the spectrum, which is due to either hematin or methæmoglobin.

If this fourth line is observed, the blood must be tested as to its reaction. If alkaline, this points to methæmoglobin; if acid, to hæmatin. The first case deserves but little attention, as a rule, unless there has been poisoning with hydrogen sulphide (which is not likely to originate from the putrefaction process),

\*From *The Analyst*, translated from the *Chemiker Zeitung*, slightly abridged.

but the second points to the administration of acids, nitroglycerin, potassium chlorate, or ferrocyanide or nitrobenzol. These bodies will then have to be searched for in the urine and other parts of the body.

In most cases, the only question is to decide whether the blood contains carbonic oxide. If we have to deal with a blood whose oxyhæmoglobin has been completely converted into the carbonyl compound, without the reverting process having set in, the detection of the carbonic oxide is easy, chemically as well as spectroscopically. If the blood, however, only shows the lines of the non-reduced or partially reduced hæmatin, the detection of the carbonic oxide is not successful, and, in fact, not likely to be so.

Not unfrequently a blood will have to be examined for carbonic oxide, when it contains carbonylhæmoglobin, oxyhæmoglobin and hæmoglobin, with perhaps methæmoglobin or hæmatin.

In such a case, the presence of the carbonyl compound can only be proved by adding ammonium sulphide, and noticing whether the absorption band moves towards the red part of the spectrum. The chemical testing with soda lye, with or without calcium chloride, is not trustworthy.

*(b) Urine.*

In testing this, it must be noticed that this fluid undergoes remarkable changes whilst the poison is acting; also that many poisons only then pass into it when their physiological action is over. Therefore ascertain, if possible, the quantity of the urine, then look at its color, notice the smell, test for blood, albumen, sugar, also its behavior towards barium chloride, both before and after addition of hydrochloric acid.

The urine may also contain volatile bodies, balsams, alkaloids, and poisonous metals; whilst if poisonous doses of potassium chlorate, iodide or bromide have been given they will be readily detected in this fluid.

*(c) The contents of the Stomach.*

After noticing the odor and reaction, try whether there is a phosphorescence in the dark. If the stomach has an alkaline reaction, any phosphorescence cannot be due to phosphorus, but is caused by a fungoid growth, for phosphorus only lights when

the contents are acid. The reaction of the contents will, according to circumstances, be acid, alkaline, or neutral. Poisoning caused by corrosive acids, caustic alkalies, or haloids, is sure to have been recognised by the medical man who conducted the post-mortem examination.

The odor will not give much information if the contents are much putrefied. But when they are apparently in a good state of preservation, I have often noticed a loathsome, sweetish smell in the case of a decided form of arsenical poisoning. If the contents are solid, it is best to take an aliquot part and digest it in a small beaker with spirits of wine, and finally wash the insoluble matter with ether. The residue must now be rigorously examined with the microscope, which will often show remnants of medicines, pills, or powders. The alcoholic solution may be tested for oxalic acid. In many cases the stomach has been washed out for the purpose of the post-mortem. In this case the sediment of the wash-water must be carefully examined. Many indifferent objects will often be found, such as particles of carbon, fragments of coffee, potatoes, grain, greens or flesh, also crystalline bodies, such as triple phosphate, if the stomach has an alkaline reaction. If seeds are found, they must be well washed with water, alcohol, and ether, sorted, weighed and examined. If particles of arsenious acid are noticed, they may, after being freed from adhering matter, be gently dried and weighed, or dissolved in solution of potassium bicarbonate, and titrated with iodine. When the microscopical investigation is over, it is, in many cases, advisable to take a little of the contents and test for arsenic first, as this is the commonest form of poison. If not found, another portion may be exhausted with water, and the filtrate be examined for soluble metallic salts, more particularly the chlorate, nitrate, iodide, bromide, ferro or ferricyanide of potassium.

## 2.—SPECIAL PART.

If the preliminary testing has given no particular indication, I start the chemical analysis. I first of all submit the organs to a fractional distillation. The residue left in the retort is then exhausted with alcohol to dissolve out any alkaloids, and then afterwards chlorinised for the purpose of testing for metallic poisons.

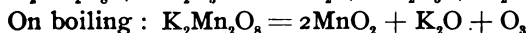
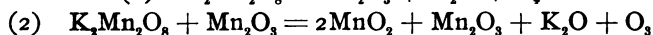
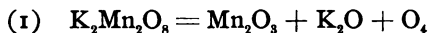
## VOLATILE BODIES.

The contents of each jar are examined separately. A portion is cut up into small pieces and put into a suitable retort containing water. The first distillation is done by immersing the retort in boiling water for several hours. I then add to the contents a little tartaric acid, and once more distil, this time by means of a current of steam. In this way we get two fractions. The first contains the readily volatile bodies, such as alcohol, aldehyde, acetone, chloroform, nitrobenzol, turpentine, camphor, amines, or their sulpho-derivatives. In the second, the remnants of the first, further, fatty acids, carbolic acid, hydrocyanic acid, phosphorus, etc. If chloral hydrate or potassium cyanide\* are suspected, the organs are moistened with caustic potash or sodium bicarbonate and distilled from the water-bath, but should it be necessary to conduct a steam distillation from an alkaline fluid, I prefer to first make an acid extract with water containing some tartaric acid, which is then filtered and made alkaline before distilling.

If the acid distillate is ready, I properly notice its reaction, color, odor, degree of turbidity, and particularly its bulk, so as to be able to make a quantitative estimation of any substance (such as alcohol) which the distillate may contain.

## THE FIRST FRACTION.

(a) Test with silver nitrate; (b) with ammoniacal ditto (aldehyde); (c) with nitroprusside, potash, and acetic acid (aldehyde, acetone). Then test with alkaline permanganate (d) as follows: 10 cc. of distillate are mixed with a few drops of potash lye, and 1 cc. of a saturated solution of permanganate, and allowed to stand for twelve hours in a closed vessel. If oxidizable bodies are present, reduction soon sets in, and the permanganate gets decolorised. The filtrate is then tested for aldehyde with ammoniacal silver. A large increase in the amount of aldehyde points to the presence of alcohol. As is well known, an alkaline permanganate acts differently in the cold than at the boiling heat. In the cold the following reaction takes place (in presence of organic matter):



\*Supposing there is also a ferrocyanide.

It is highly probable, although not yet proved, that in the cold the liberated oxygen will first act on any organic matter before peroxidising the manganic oxide.

(e) With iodine and potash lye as follows : In a test-tube I introduce a pinch of iodine, then 10 cc. of the liquid and 3 drops of a 30 per cent. potash, then heat to 50° C., when, owing to the formation of iodoform, the liquid will get more or less turbid. If the iodine is used up, a little more of it must be added, and its excess finally be removed by cautious addition of potash lye. As iodoform does not always separate in well defined crystals, the best thing is to agitate the solution with ether allowing the latter to evaporate. If after a microscopical examination of the residue there is still a doubt, Lustgarten recommends the treatment of the crystals with resorcin and potash to get rosolic acid. (f) With resorcin and potash (chloroform). I have slightly modified Lustgarten's test. In a tube introduce a pinch of resorcin, 10 cc. of the distillate, 3 drops of a 30 per cent. potash lye, and warm gently, when the beautiful rosolic acid is soon formed. This test is more delicate than the isonitril test ; then, however powerful and characteristic the smell may be, it is often masked by the presence of amines. In regard to the prussian blue test (treatment of chloroform with alcoholic ammonia and potash), although when performed under pressure a good result may be obtained, this test is far inferior to the rosolic acid test. (g) Zinc dust and hydrochloric acid (nitro-benzol). 10 cc. of distillate are mixed with an equal volume of 90 per cent. alcohol, a little zinc dust is added, then 1 cc. of hydrochloric acid, and a drop of platinic chloride. After standing for three hours, the liquid is decanted from the undissolved zinc and the greater part of the spirit driven off on the water-bath. The residue is now diluted with water, rendered alkaline with potash, and shaken out with ether. The ether is evaporated, and the residue tested for aniline with freshly prepared solution of chloride of lime, which will produce a blue color should nitro-benzol have been present. (h) With hydrochloric acid and alcoholic solution of phloroglucin (ethereal oils). This test, proposed by Ihl for the detection of bodies of an aldehydic nature, will often give unreliable results when applied to the distillate of portions of bodies, but it is best applied to the

distillate of the urine. Hager's test for oil of turpentine is best carried out as follows: A pinch of guaiacum is dissolved in 1 cc. of absolute alcohol and 5 drops of oil of lemon and the mixture boiled; 10 cc. of distillate are added, and the whole boiled once more. The test only succeeds when notable quantities of turpentine are present, and the reagent must be quite fresh. If, however, the distillate should have no action on alkaline permanganate or solution of chromic acid, ethereal oils are out of the question.

A quantitative estimation of these volatile bodies will not often be practicable, not so much because no proper processes exist, but chiefly on account of the scarcity of material. An exception, however, is the estimation of the alcohol. Any one who has often had occasion to quantitatively determine alcohol in poisoning cases will often wonder how it is so comparatively little attention has been paid to this subject in the works on toxicology and even chemistry. Rarely will the contents of the stomach be in such a fresh condition and the amount of alcohol so large as to admit of the estimation of the alcohol by the usual process, viz., distillation and specific gravity, more particularly as the gravity may be altered by the presence of amines. Even addition of mineral acids or even platinic chloride and redistilling will not altogether remove the organic bases. The only way is to oxidise the alcohol to acetic acid and to estimate this volumetrically. I carry out this estimation as follows: The distillate is once more distilled off. What passes over in the first quarter of an hour is collected in a receiver containing some dry potassium carbonate. The process is repeated until we finally have a distillate measuring about 10–20 cc., mostly strongly ammoniacal. It is put into a high-pressure flask, mixed with 3 cc. of a 20 per cent. solution of potassium bichromate, and, after being placed in a freezing mixture, mixed with about 10 cc. of strong sulphuric acid, or more if the iodoform test has been very successful. After closing the flask, it is heated in boiling water for eight hours. After cooling, the contents are put into a flask (kept cool), supersaturated with potash, and boiled until every trace of compound ammonia has completely disappeared, which is readily ascertained by exposing to the vapours a piece of red litmus paper.

After acidifying the solution with sulphuric or phosphoric acid, it is distilled (by means of introducing steam) until the distillate is no longer acid. The distillate, often measuring a liter, is titrated with  $\frac{n}{10}$ -soda, using *litmus* as indicator. The alcohol is then calculated from the amount of acid found, and it must then be recalculated to the original volume of the distillate. To make sure the distillate really contained acetic acid, the neutralised fluid is boiled down to a small bulk. An aliquot part is tested with barium chloride, and should there be any precipitate, it must be collected and allowed for. Another portion is mixed with a few drops of alcohol and then with sulphuric acid in excess. If after twenty-four hours there is a strong odor of acetic ether, the presence of acetic acid, therefore the presence of alcohol is proved beyond doubt. Or we may apply Carstanger's well-known cacodyl test.

The principles of the method just described will be easily understood. I must, however, point out the absolute necessity of thoroughly boiling the oxidised mixture with potash, otherwise the process is bound to fail. The amines always pass into the alcoholic distillate, even if distilled from an acid solution. They are not acted upon by the oxidising mixture, and, therefore, unless removed by boiling with caustic potash, they would again get into the acetic distillate.

As already stated, not much importance seems to be attached to the qualitative and quantitative toxicological determination of alcohol; not so much because there are no reliable processes, but principally because it is only reckoned a poison in its pure state. I hold, however, a quite different opinion. Think how alcohol in its various forms, from brandy to methylated spirits, is within almost everybody's reach, and how easily it may be abused; not so much in the case of grown-up people, but helpless infants. Is it not a well-known fact that gin, for instance, is largely administered to infants to make them sleep, and how many have not in this way been killed by their unnatural mothers, without these in the least being suspected: Are not two tablespoonfuls of corn brandy often a *fatal* dose for a child of six months old? Is it not probable that among the lower classes this comparatively safe way of infant poisoning is largely practised? The chemical detection

of alcohol is beset with difficulties ; then first of all it rapidly passes out of the system, and it has also been proved that traces are actually formed in the living organism, whilst it is even a product of putrefaction. I therefore must insist upon the quantitative estimation of the spirit, which, if the amount should be excessive, will point to the use of alcoholic liquors, or even tinctures, or may be in other respects a valuable clue.

The following observations, which I have made during my search for alcohol in the various organs from persons who were confirmed drunkards, will be of interest. The organs did, however, not reach me for a week or a fortnight. 1. Pure ethylic alcohol was found in a few cases. From the contents of each jar containing respectively the stomach, duodenum small intestine ; the pieces of the large glands of the abdomen ; the lungs and brain, I have always succeeded in getting alcoholic distillates, but I never succeeded in getting alcohol or aldehyde from the urine. In many cases (it was not known whether the persons had partaken of alcoholic liquors shortly before death) I noticed the interesting fact, that whilst the distillate from the stomach was absolutely free from alcohol, the liver, kidneys, spleen, yielded a distillate containing it. In one case the reaction of the stomach was acid, and in the other faintly alkaline. The distillates when containing alcohol, give the following reactions :

1. Alkaline permanganate is reduced in the cold ; the filtrate reduces ammoniacal silver nitrate.

2. A mixture of potassium bichromate with sulphuric acid is also reduced. The mixture has either the odor of aldehyde, acetic acid, acetic ether, or a pungent odor of rum, or often of a fruit essence.

3. A more or less strong iodoform reaction will be got.

4. If a few drops are collected at the beginning of the second distillation (over dry potassium carbonate), these will burn with the characteristic alcohol flame. This beautiful (but not very conclusive) test may even succeed when the organs are in an advanced state of putrefaction, but it will have to be conducted with great care, and best in a dark room. Before setting light to it, the crucible containing the spirit must be slightly warmed. The drawback to this test is the waste of the greater part of the spirit.



The cases where alcohol was only obtained from the liver and spleen, whilst none could be got from the stomach, etc., seem to me very peculiar. It is not improbable that the alcohol was formed by a kind of fermentation of the glycogen contained in the liver. It is also difficult to explain how it came that in one case where the medical men conducting the post-mortem, recognised alcohol by its smell, and certified as to alcoholic poisoning, no ethylic alcohol was found, but its higher homologues. This, however, was after a lapse of eight days between the inquest and the analysis. This strange fact may perhaps be explained by the great volatility of ethylic alcohol, causing it to evaporate even from the dead organism. The following experiments, which I made to show the volatility of even dilute alcohol, proved interesting :

In a beaker 75 mm. square, I put some very dilute alcohol, and allowed it to spontaneously evaporate, estimating the percentage of alcohol from time to time by means of the vaporimeter. The results were as follows :

On December	20,	1886,	the liquid contained 2.4 volumes of alcohol.			
" "	21,	" "	"	2.0	"	"
" "	24,	" "	"	1.4	"	"
" "	27,	" "	"	.75	"	"
" "	28,	" "	"	.60	"	"
" January	10,	1887,	"	.20	"	"
" "	22,	" "	"	.0	"	"

The beaker still contained water.

From these experiments it is plain that alcohol rapidly evaporates even from dilute solutions. If one now considers how clumsily post-mortems are sometimes conducted, it can scarcely be a matter of surprise, that the alcohol has in many instances completely evaporated before the organs reach the analyst. In conclusion, I may mention that the largest quantity of alcohol I ever found in a stomach did not exceed .02 gm., whilst the other organs yielded still less of that substance.

#### THE SECOND FRACTION.

##### (a) *Carbolic Acid.*

As this body is always among the products of the putrefaction of albumenoids, one will generally find a trace of it with Millon's

reagent\* or (though not so frequently) with bromine water. If a poisonous dose is present, its amount may be estimated in a satisfactory manner, as follows :

The distillation is carried on until what passes over gives no coloration with ferric chloride. Not to lose any, it is advisable to continue the distillation until no coloration is got by Plugge's test. Both distillates are now filtered off from any fatty matter, and separately shaken out with *pure* ether. The total ether is now allowed to evaporate, and the residue is titrated in the well-known manner with bromine water and hypo.

(b) *Prussic Acid.*

Before applying any other test, I first use a strip of filter paper dipped first in a very weak solution of copper sulphate, and then in freshly prepared tincture of guaiacum. If the (tartaric acid) distillate contains prussic acid, the paper when moistened with it will turn blue. If no coloration is got, it is quite superfluous to try any other tests, but if obtained, it is as well to try and get the prussian blue, the sulphur, and also the nitroprusside test. As regards the prussian blue test, I must emphatically warn against using too much ferrous sulphate, as otherwise a yellow color will almost completely obscure the blue. If the amount of prussic acid is very small, a precipitate will sometimes take a long time to form. When applying the sulphur test, the great thing is to avoid an excess of ammonium sulphide.

If prussic acid has been found, one must not neglect to test the residue in the distilling flask for possible ferrocyanides.

A quantitative estimation of the prussic acid is conducted as follows : The distillate is, if necessary, acidified with nitric acid, and precipitated with silver nitrate. The precipitate is collected on a weighed filter, washed, dried and weighed. To make sure, the precipitate is ignited, and the residual silver also weighed.

(c) *Phosphorus.*

To observe very plainly the glowing of the phosphorus, I must recommend the use of the bulb-tube. The vapors for a long time condense in the bulb, which, in consequence, will appear quite luminous. If the phosphorescence vanishes, it may be several

\*Note by translator. A solution of mercurous nitrate containing nitrous acid ; first used by Professor Plugge for the detection of phenol and allied bodies.—L. de K.

times made to again appear by opening the steam apparatus for a moment (and temporarily removing the flame) so as to let a little air get in. After distilling for about an hour, the distillation is stopped. All the while the receiver must have been kept very cool and also connected with a U tube containing solution of silver nitrate. After particularly noticing whether there are any globules of phosphorus, the liquid may be tested for phosphoric acid by means of chlorine water and ammonium molybdate. A quantitative estimation may be attempted, but only about half the original phosphorus will, as a rule, be found. If no phosphorus has been detected, it must not be omitted to test the residue in the retort for *phosphorous* acid, say by Dusart-Blondlot's process.

#### ALKALOIDS AND ALLIED BASES.

The testing of organs for alkaloids is, as is well known, one of the most difficult chemical problems, which fact will be admitted by every analyst of long standing and experience. Our imperfect knowledge of the ptomaines, and the conditions necessary to their formation and disappearance, makes it so difficult to judge about the alkaloidal nature of a substance. There has already been such an amount of literature about ptoma-conine, ptoma-strychnine, etc., that I should not wonder to notice one of these days a pamphlet on the preparation of strychnine, morphine, etc., from putrefying white of egg. It is argued, with much truth, that a nitrogenous base, isolated from organs, is only then to be pronounced a vegetable alkaloid when it possesses *all its physical, physiological and chemical properties*. Of course, in such a case, there is no fear of its being a ptomaine; but alkaloids are generally present in such small quantities, that it is mostly impossible to get *all* reactions satisfactorily, and I feel sure that many a too-particular analyst has in consequence been induced to call vegetable alkaloids ptomaines.

It certainly is much easier, in the present state of science, to pronounce a residue to be a ptomaine instead of an alkaloid, for the simple reason that one rarely ever succeeds in isolating the base from the organs in a *perfectly pure condition*.

The best way to extract the alkaloids is by means of an alcoholic solution of tartaric acid. The fat which separates out

scarcely deserves any further attention, although it is not quite impossible that it may act as a solvent for organic poisons;\* but it mostly consists for the greater part of cholesterin. The extracts got from a stomach are mostly of a bright yellow color, more particularly if there was an abundance of bile; but organs containing much blood give extracts of a much darker color, and should therefore be analysed separately.

A clarification of the solution may be attempted by adding alcoholic solution of tartaric acid as long as a precipitate forms. The filtrate is evaporated, the residue taken up with water, and then nearly neutralised with potash. On adding alcohol, the potassium tartrate is precipitated, carrying down a good deal of the coloring matter.

After evaporating off the spirit, the watery fluid is once more tested as to its reaction, and, if necessary, neutralised with potash. As it is difficult to get perfect neutrality, it is best to use very delicate litmus paper, working until only the faintest acidity is noticed. Before using the regular course, one must never omit to test a little of the solution for meconic acid, and also to notice its behavior towards iodic acid. If no iodine is liberated (acidify the fluid with tartaric acid), it is no use trying for morphine; but of course a separation of iodine does not in the least prove the presence of that alkaloid, as other bodies may cause the reaction. The fluid is now divided into three parts. Part 1 is made alkaline with potash and distilled in a current of steam or hydrogen. The distillate is to be especially tested for nicotine, conine, and aniline, which is done best by first shaking it with ether and evaporating this in a current of air, the flask containing the solution being surrounded with water of 70–80° C. When about 10 cc. of ether are left, it is put to spontaneously evaporate in a small beaker. The residue is dried in vacuo over sulphuric acid, and then made into a neutral hydrochloride.† If necessary, the usual tests for nicotine may be supplemented by preparing the double salts with gold or platinic chloride, and submitting these to a quantitative analysis.

If no volatile bases have been found, the second portion is

\*For instance, nitroglycerine. In the absence of fatty matter, this is best isolated by extracting the air-dried substance with chloroform, finally drying the extract over sulphuric acid.

†Conine hydrochloride is of characteristic appearance.

shaken out : 1. With ether, both from acid and alkaline solution. 2. With chloroform from alkaline solution. 3. With amylic alcohol after addition of ammonium chloride, but this is only necessary if the iodic acid test has been successful. Before shaking with the chloroform, any ether must be expelled by gentle warming and blowing, and before using the amylic alcohol, any chloroform must be likewise got rid of.

If reactions are got which point to the presence of a particular alkaloid, a special process is applied to the third part of the fluid. It is a good plan to add solution of mercuric chloride, which precipitates every trace of nitrogenous base in twenty-four hours. The deposit is washed with a weak solution of sublimate, and the alkaloid is then isolated in the usual manner. The residues left after evaporation of the ether, chloroform, and amylic alcohol must always be dried over sulphuric acid; they are partially amorphous and crystalline, colorless, or of a yellow or brown color. Froehde's reagent is often reduced with a blue color, to which, however, not much importance must be attached. The same may be said of the passing green color obtained with a sulphuric acid solution of ammonium vanadate. The residue from the alkaline ether will nearly always get violet on warming with syrupy phosphoric acid, although this test has been supposed to be characteristic for aconite only.\* The otherwise so splendid atropine test of Vitali (treating the pure alkaloid, first with fuming nitric acid, and then with alcoholic potash) will, however, mostly fail with the impure residue. The same failure is sure to occur on applying the chromic acid test (getting an agreeable odor).

As a test for strychnine, ammonium vanadate has lately been strongly recommended and found trustworthy. The experiment is best performed in two ways. First of all, the solution of the vanadate in sulphuric acid is dropped on to the alkaloidal residue; and, secondly, solid vanadate is first added, and the whole moistened with sulphuric acid. This test is preferable to the time-honored test with bichromate, at least, when the alkaloid is somewhat colored.

\*Note by Translator. I have often seen syrupy phosphoric acid turning violet on heating, most likely caused by some organic matter.

I must now call attention to an important fact, as far as I am aware, not yet published, viz.: Colocynth resin gives with vanadate solution a reaction almost like strychnine.

If this drastic (colocynth) is suspected, I proceed as follows: The residue is mixed with a pinch of powdered bichromate with addition of a few drops of dilute sulphuric acid (1-2). At a little distance, a little strong sulphuric acid is placed, and the two liquids drawn together with a glass rod. A beautiful violet red is thus obtained, which gradually increases in color. If vanadate is used instead of bichromate, a blue color is first obtained and a violet-red afterwards.\*

The residue obtained by evaporation of the amylic alcohol (which must first be passed through a dry filter) is often impure, and is best purified by treatment with alcohol. The morphine is then tested for by the ordinary reagents, or it may be tested after conversion into apomorphine.

#### METALLIC POISONS.

I either use the residue from the distillation or the residue from the extraction with alcohol, in which case the latter is expelled by gentle heat. After adding boiling water and a sufficiency of potassium chlorate, hydrochloric acid is gradually added until the organic tissues are disintegrated. I am sorry to say I cannot recommend Jeserich's plan of using chloric acid, as this seems never to be quite free from arsenic, otherwise it is an excellent process. After warming for some time to expel chlorine, if necessary with an occasional addition of hot water, a little tartaric acid is added to keep up any antimony, and the whole set aside for twenty-four hours.

##### (a) *The insoluble portion.*

This is collected on a filter and washed with water until the washings are colorless (if there should be a large residue, it is a good plan to once more treat with chlorine), then with alcohol, and finally (in a beaker) with ether, until the fat is practically removed. The residue is now burnt in a porcelain dish. The ash is first digested with weak hydrochloric acid and the insolu-

\*Note by Translator. This is very nearly the same as with strychnine, showing, after all, the advisability of always using the chromate reaction when testing for strychnine.

ble ash collected, washed, dried, ignited, and weighed. If it should not merely look like sandy matter, its nature must be investigated, best by fusing it with (previously ignited) sodium bicarbonate in a platinum crucible. After treating the mass in water, any insoluble matter is dissolved in nitric acid, and the solution tested with hydrochloric acid (silver), sulphuric acid (lead, barium, strontium), and hydrogen sulphide. The alkaline filtrate is mixed with excess of hydrochloric acid and evaporated to dryness (to render silica insoluble). After taking up with acid water and filtering, the liquid may be tested for alumina. In a case of poisoning by barium chloride, where sodium sulphate had been given as an antidote, I could not find any barium in the stomach, œsophagus, and duodenum, but got as much as .158 gm. of barium sulphate from the abdominal glands, brains, and lungs, whose joint weight was 719 gms.

(b) *The soluble portion.*

I must state that it is absolutely necessary that the fluid shall contain no free chlorine. After making up a definite bulk, say 500 cc., aliquot parts are taken and submitted to analysis.

(a)

50 to 100 cc. are nearly neutralized with caustic potash in a porcelain dish, a small coil of clean brass is introduced, and the whole warmed for fifteen minutes. The coil is then washed with water, alcohol, and ether, and after drying (in desiccator) introduced into a combustion tube partly filled with coarse oxide of copper, and drawn out so as to be connected with two capillary tubes. By means of an aspirator, a slow current of dried air is drawn through and the tube heated as if an elementary analysis were conducted. Any mercury will condense inside the capillary tubes.

Whilst still hot, a drop of water is put on the combustion tube (close to the capillary one) and is so made to break. A minute particle of iodine is now introduced, and with the application of a gentle heat, its vapor mixed with the air current, is made to act on the mercury globules, which will then cause the formation of the characteristic mercuric iodide. As regards this very reliable process, I want to observe that the long immersion of the brass is

not advisable, because it gets too thickly coated with organic matter.

The quantitative estimation of the mercury I conduct as follows: Through the hot acid solution I pass hydrogen sulphide, and collect the precipitate on an asbestos filter. After washing with strong hot hydrochloric acid, the asbestos is rinsed into a beaker and digested with a few drops of nitric acid, which will soon dissolve out the mercury. After filtering through the same asbestos, the mercury is precipitated as mercurous chloride by the addition of excess of phosphorus acid, which is allowed to act for twenty-four hours.

(b) *Antimony.*

50 cc. of the liquid are put into a clean platinum dish, the excess of acid neutralised with ammonia, and a piece of pure zinc is introduced. After acting for six hours, the liquid is poured off and the antimony will have blackened the platinum, or, if much was present, deposited itself as a spongy mass. The liquid may contain traces of it, as antimony is somewhat soluble in concentrated solution of zinc chloride. Its quantitative determination is conducted as follows: Through the hot liquid I pass hydrogen sulphide until the liquid has got cold. After standing for three days, the excess of hydrogen sulphide is removed by a rapid current of carbonic acid, a little ether being, if necessary, added to prevent frothing. The precipitate is filtered off and washed with a weak solution of ammonium acetate. It is then rinsed from the filter with solution of caustic soda, which is then saturated with hydrogen sulphide, which will cause the antimony to dissolve. After filtering off from any insoluble matter, the liquid is slightly acidified with hydrochloric acid and heated to boiling. After standing for a day, the precipitate is filtered off, washed, and finally oxidised with nitric acid. To completely get rid of organic matter, the mass is made alkaline with caustic soda, dried and fused with a mixture of nitrate and carbonate of soda. The mass is now exhausted with proof-spirit, and the insoluble sodium antimoniate washed with proof-spirit to which a few drops of sodium carbonate have been added. It is then digested in a mixture of hydrochloric and tartaric acids, the liquid nearly neutralized with ammonia, and once more precipitated with hydrogen sulphide.



The precipitate, which should now possess the characteristic color of antimony sulphide, is not weighed as such, but I prefer to convert into oxide by treatment with fuming nitric acid, taking all precautions as advised by Bunsen.

To make sure of the absence of tin, I place the uncovered crucible in the reduction flame of a powerful burner, when the antimony will gradually, but completely, volatilise.

*(c) Detection and Estimation of Arsenic.*

If no mercury or antimony are present, 50 or 100 cc. of the liquid are put into a Marsh's apparatus and tested for arsenic. The zinc must be first put into hydrochloric acid for ten minutes, and then washed with water, in order to free it from traces of adhering arsenic. Of course before lighting the hydrogen or heating the reduction tube, one must wait until all air has been expelled. The liquid must be introduced in small quantities, otherwise there may be too much frothing. It is as well not to try and get arsenical spots, as these only form well when there is a rapid evolution of hydrogen and a large quantity of arsenic; but it is best to produce the arsenical mirrors, which may afterwards be sealed if necessary, and produced as evidence in court.

If the amount of arsenic was not too small, and one has succeeded in getting at least two mirrors, the tube is cut with a diamond in such a way as to get four pieces of the mirror. The following tests are then applied: One piece is heated and the arsenical odor observed. The second piece is moistened with sodium hypochlorite, when the mirror should of course disappear. The third piece is treated with nitric acid, and, after evaporating the acid, the residue is tested with silver nitrate for arsenious or arsenic acid. The fourth piece is heated with ammonium monosulphide, and the arsenic made into the yellow sulphide. These four tests are amply sufficient.

If arsenic has been found, it is quantitatively estimated as follows: The liquid is warmed and treated for twelve hours with hydrogen sulphide, then put aside in closed flask for about five days, until the precipitate has completely settled. After removing the excess of hydrogen sulphide by a current of carbonic acid, the precipitate is filtered off and washed. The filtrate, as a rule,

gets turbid, but one need not pay much attention to this, as the cloudiness *may* be due to a trace of arsenic, but is generally caused by organic matter.

To purify the precipitate, it is best to use a solution of ammonium carbonate, which will leave at least the bulk of the free sulphur behind. After evaporating the solution, the residue must be treated with nitric acid, the solution evaporated, and the product fused, best in a porcelain crucible, with a mixture of nitre and potassium—sodium carbonate. After dissolving the mass in water, it is best to slightly acidify with nitric acid, and after completely removing the carbonic acid and nitrous acids by boiling, once more to throw down with hydrogen sulphide. The precipitate must then again be converted into arsenic acid,\* and the solution, after concentration, be precipitated with magnesia mixture. To make sure of its purity, it is as well to redissolve the precipitate after slight washing with dilute ammonia, in hydrochloric acid, and once more throw down with ammonia. I have adopted with great success the proposal of de Koninck,† who dissolves the arsenical precipitate off the filter by means of nitric acid, evaporates the solution, and gradually heats the residue to redness. The pyroarsenate may be kept, or if there is not much of it, may be made into mirrors of metallic arsenic by means of the Marsh's apparatus, in the way already described.

(d) *Tests for Other Metals, Tin Excepted.*

If mercury, antimony, and arsenic are absent, the liquid is made alkaline with *pure* sodium hydrate, then acidified with acetic acid, and, after heated to boiling, treated with hydrogen sulphide until it is cold. Sodium carbonate is now added until alkaline reaction, and the corked flask set aside until the liquid has become quite clear. After collecting the precipitate (which, as a rule, consists mainly of ferrous sulphide) on a filter, it is washed with solution of sodium hydrogen sulphide until the washings run off colorless. The filtrate is kept for further investigation. The precipitate is now put into a porcelain dish, cautiously oxidized with nitric acid, and the acid evaporated off. The residue, after being moistened with a drop of strong soda, is mixed with a little

\*Note by Translator. Very conveniently done with bromine water.

†See *Analyst*, 1888, p. 178.

dry sodium carbonate and put by degrees into a silver crucible containing fusing nitre. After cooling, the fused mass is exhausted with water, the alkaline fluid saturated with hydrochloric acid (in a beaker), and filtered off from traces of silver chloride through filter paper, but if permanganate should be present, through asbestos, the liquid is then qualitatively and, at the same time, quantitatively analysed by the usual methods.

About the metals, which are not precipitated by hydrogen sulphide from their acid solutions, I want to make some observations. As a rule, the separation of iron, zinc, and aluminum in presence of phosphates of lime and magnesia will have to be carried out. I proceed as follows: The hydrochloric solution of the sulphides is, after evaporation, mixed with some chlorine water and again concentrated. The residue is treated with slight excess of ammonia, which throws down the phosphates, the filtrate is acidified with acetic acid, heated to boiling, the zinc thrown down with hydrogen sulphide, and the zinc sulphide collected on a weighed filter. The phosphatic precipitate, which may contain alumina, is dissolved in nitric acid and heated in a platinum dish with metallic tin, which will cause the separation of phosphoric acid as stannic phosphate. The filtrate is precipitated with ammonia, and the precipitate, after washing, burnt together with the filter. The ash is then fused with caustic soda for half an hour, which will form aluminate of soda, from which the pure alumina may be isolated in the usual way, after first extracting the alkaline mass with water, and filtering from any insoluble matter.

*(e) Estimation of Tin.*

The sodium sulphide solution is acidified with hydrochloric acid boiled and treated with hydrogen sulphide. After twenty-four hours the precipitate is filtered off and washed with solution of ammonium acetate. The filter and contents is then heated in a porcelain crucible until the sulphide of tin has been converted into oxide, which oxidation may be assisted by the use of nitric acid. As, however, the oxide may contain traces of iron, it is best to fuse it in a silver crucible with pure caustic soda (free from water) for half an hour, at a temperature just high enough to melt the soda. After exhausting the mass with water, the liquid

is filtered, acidified with hydrochloric acid and the tin precipitated with hydrogen sulphide. The stannic sulphide is then converted into oxide and finally weighed.

#### FINAL REMARKS.

Among the normally occurring metals of the human body must be reckoned potassium, sodium, calcium, magnesium, iron, and manganese. But one is sure to find, also, aluminum, copper, zinc; even tin and lead. Of the last four there is, however, seldom more than one centigram. in a full-grown body. Traces of these metals, of course, get into the organism through the use of contaminated food, or impure beer, etc. If more than a trace is found, inquiries should be made whether the deceased has been habitually taking medicines containing doses of, say, mercury or lead, or even, arsenic. As regards alumina (considering this is a constituent of sandy matter, clay, dust), traces of this substance may even get into the organs during the post-mortem examination, which, as we all know, is sometimes not too neatly conducted. As is well known, the organic matter rendered soluble by the treatment with chlorine is precipitated by hydrogen sulphide both in acid or alkaline solution. The removal of this organic matter by fusion with nitre answers very well for arsenic, antimony, and tin, but suppose there were mercury, this would volatilise. As I, however, test for mercury first by a special process, there is no danger of not finding it.

Contrary to the usual plan, I test for arsenic directly in the acid liquid, and only *then* proceed in the conventional way when the organs contain decided traces of free nitric acid, mercury, or aniline colors. Notwithstanding Otto's objections, I prefer this direct way of testing, which in fact had already been recommended by Marsh himself. It saves the troublesome treatment with hydrogen sulphide, which substance has lately become somewhat notorious as a possible source of arsenic.

To ascertain the influence of nitrates, I carried out the following experiment: From a weak hydrochloric acid solution of .75 per cent. nitre and .33 per cent. arsenious acid, I added 1 cc. to portions of organs, which were mixed up with water containing 5 gms. of potassium chlorate. After treating with acid as described, and freeing the filtrate completely from chlorine, the liquid was

tested in the Marsh's apparatus, in which hydrogen was evolved from zinc and hydrochloric acid. After eight hours, practically all the arsenic had deposited in the reduction tubes. I must observe that addition of sugar seemed to favor the reaction.

From this experiment it seems that the presence of chlorides, even nitrates, does not interfere with the formation of gaseous arsenic hydride, at least when there is plenty of zinc and acid, and sufficient time is allowed. Besides, as nitre speedily passes into the urine, no quantity of nitrate to speak of will ever be present in the organs when they are being tested for arsenic.

I further made a second experiment to ascertain the influence of free nitric acid. A small quantity of arsenical liquid was put into the Marsh's apparatus, and a mirror was soon obtained. When nitric acid was added, the generation of arsenic hydride seemed to cease, but it began to reappear after about twenty minutes, when no doubt all the nitric acid had been reduced.

Much has been said about the formation of solid arsenic hydride in presence of nitric acid, but it is still doubtful whether in presence of zinc and hydrochloric acid this does not gradually pass into the gaseous state.

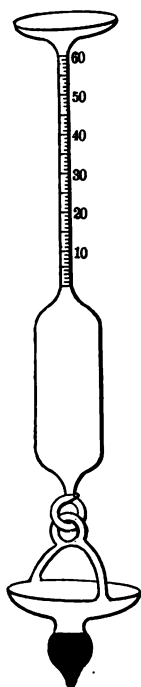
In conclusion, I wish to remark that, although as a rule, only a single poison needs to be searched for, many poisons contain two or even more deadly constituents. For instance, imperial green, chrome-yellow, medicinal tinctures, etc. How often has it not occurred, that the more or less inebriated condition of a person has given his companion a chance of giving him a supposed pick-me-up? I once had to test a stomach for alcohol, and indeed this body was found, but I also succeeded in isolating weighable quantities of arsenic. It was therefore probable this victim had been poisoned whilst in a state of intoxication.

#### A NEW FORM OF HYDROMETER.\*

By G. H. FAILYER, Kansas State Agricultural College, Manhattan.

The writer has had charge of a large class in determinative mineralogy, and found it inconvenient and expensive to supply them with sufficient appliances for getting the specific gravity of the minerals. The Jolly balance answered a good purpose, the errors in its use not being greater than the variations in

\*From the Transactions of the Kansas Academy of Science.



the gravity of the minerals themselves. But the price of the balance led to the wish for something equally rapid and accurate, and of such price that a number of them might be placed at the disposal of the students. He therefore devised a combination of the Nicholson and the Beaumé hydrometers, such that the work can be done with more satisfaction than with the Jolly balance, and the instrument is quite inexpensive. The accompanying cut will fully show its form.

It was neatly made for me by E. Greiner, of New York. Its essentials, of course, are the two pans and the graduated stem. The more slender the stem, the less, proportionately, the error in reading.

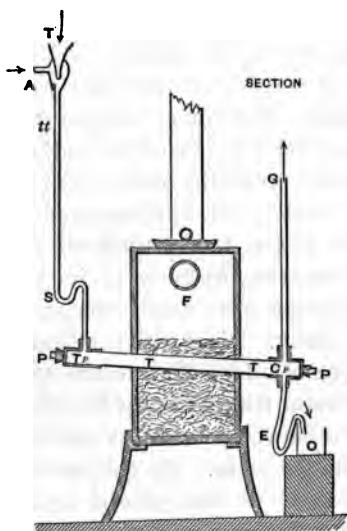
Its use is almost obvious from the instrument itself. There is no fixed water line, but the graduation extends somewhat below the surface of the water as the unloaded instrument floats in its jar. The readings and calculations are exactly similar to those made in using the Jolly. First, the position of the instrument in the water is noted. This is best done by reading through the water (that is, at the lower instead of the upper surface of the film separating the water and the air), where the plane of the water cuts the stem. By this means, the meniscus gives no trouble. The solid is then placed in the upper pan and another reading taken. A third reading is taken, this time with the substance in the lower pan. The first reading subtracted from the second will give a number representing the weight of the substance; the third from the second, the displaced water. The gravity is then found in the usual way.

By making the stem small, the accuracy of the instrument is increased. In a comparison of one with the Jolly balance, I obtained these results with the same piece of barite: With the Jolly, 4.519, 4.523, 4.471, average 4.504, greatest difference .052; with the new hydrometer, 4.474, 4.475, 4.460, average 4.469, greatest difference .015. But it is not claimed that results are more accurate by this instrument than by the Jolly balance. It is cheaper and more convenient. I have observed that where both are accessible to students, they will use the hydrometer in preference to the balance.

# ABSTRACTS.

## APPARATUS AND REAGENTS.

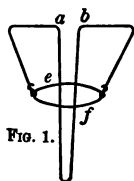
**A Simple Gas Generator.**—F. W. Boam, Chem. News 61, 244.



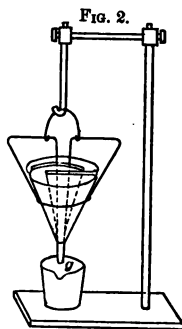
The apparatus consists of an ordinary circular or square cast-iron stove or furnace *F*, through the body of which passes a short length of  $1\frac{1}{2}$  or 2 inch iron pipe *T*. This pipe is plugged at each end, *pp*, while at the upper end is a T piece *Tp*, and at the lower is a "four-way socket" *Cp*. The plugs admit of the tube being readily cleaned. Into the *T* piece is fitted a narrow tube, about  $\frac{1}{8}$  inch bore, having an S shape bend towards the lower end *S*. At the top it widens, admitting the nozzle of a funnel *T*, and the end of a branch tube *A*. Into

the bottom branch of the "four-way socket" *Cp* is fixed a tube with a syphon bend *E*, underneath which is placed a receptacle, *O*, to catch any surplus oil, while into the upper branch of *Cp* is screwed a pipe *G*, to carry the gases to the gas-holder. Paraffin oil or any fluid hydrocarbon, is dropped from a vessel placed above the funnel *T*, into the funnel, and thence down the pipe until it overflows at *E*. When this occurs, the fire is lighted in the furnace *F*, and the oil supply is regulated so that each drop carries with it a small bubble of air. When *T* becomes hot, gas will be generated, and is carried through the pipe *G* to the gas-holder, which is most conveniently of the sheet-iron form, suspended in water, and counter-balanced by a weight. A. H. W.

**Filtering Arrangement.**—C. R. Gyzander, Chem. News 60, 167. The author describes an improvement on Mr. Fessenden's arrangement for rapid filtration (Chem. News 60, 102, this Journal 3, 414). The filter support (fig. 1) is made from platinum,

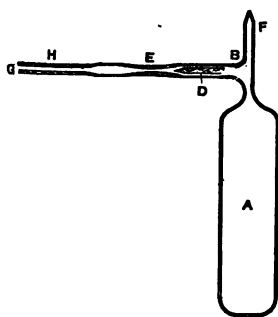


copper wire, or other suitable material, bent as shown in the figure. The paper is folded as described by Mr. Fessenden, and is pushed between the wires *a* and *b* (Fig. 1), which answer the same purpose as the glass rod, viz., to support the inner folds of the paper, while the ring *ef* supports the outer folds. The arrangement may now be placed in a glass funnel, or used alone, by simple suspension over a beaker (Fig. 2), the liquid dripping from the wire at the point *g*. A glass rod bent as in Fig. 3 answers very well. A support of  $\frac{1}{32}$  inch platinum wire, with the ring *ef*  $2\frac{1}{8}$  inches in diameter, and the wires *a b* 3 inches long serve admirably for a  $7\frac{1}{2}$  inch filter. This method affords a much more rapid and convenient way of drying precipitates than the old way of drying in a glass funnel.



A. H. W.

**Arrangement for Sealing Tubes under Pressure.**—A. Richardson, Chem. News 61, 255.



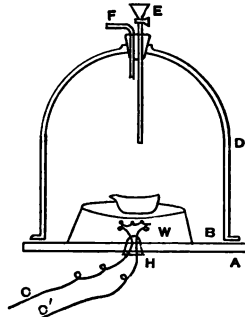
The tube *A* is joined to a T piece *B* drawn out as shown in the figure. *D* is a glass plug, ground into the tube at *E*, and acts as a valve opening inwards. When gas under pressure enters at *G*, the valve opens, but closes at once when the pressure from without is removed. The escape of gas from *A* is thus prevented, and the tube may be sealed at *H*. When the tube contains a liquid, the plug should be moistened with it, and greater care in grinding the plug is necessary in the absence of a liquid. *F* serves for the admission of



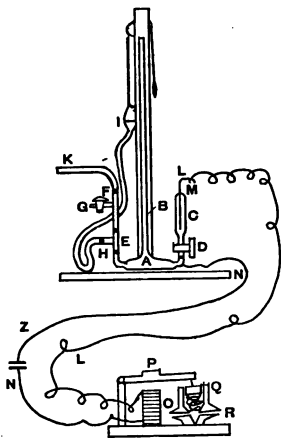
liquid into *A* in the first instance, when it is closed, and at the end of the experiment is opened to remove contents of the tube. The rest of the apparatus is untouched, and may be used repeatedly, provided the tube at *H* is fairly long. A. H. W.

**Electricity in Chemical Manipulations.**—Reginald Fessenden, Chem. News 61, 4.

(1) *Apparatus for Rapid Evaporation in Vacuum.*—*A* is a glass plate with a hole in the centre, through which a cork *H* is inserted. *GG* are two wires running through the cork, each connected to one end of the platinum loop *W*, which is packed with magnesia or a similar material. In operation, the dish *C*, containing the solution to be evaporated, is placed on the stand *B*, the bell jar is placed over all, the tube *F* is connected with the filter pump, and the wires *GG* are attached to the terminals of the battery. The evaporation is rapidly carried on, and more liquid added from time to time, through the separatory funnel *E*.



(2) *Automatic Heat Regulator and Air Thermometer.*—*A* is a piece of glass tubing, 4 inches long and 1 inch in diameter, with three nipples, one connected with a piece of thermometer tubing *B*, one to a short piece of tubing *C*, drawn out very fine at *D*, where there is a stop-cock, and the third to the T-piece *E*. *K* connects with the air bulb, *I* is a bottle of mercury, connected by rubber tubing with *H*. *N* is a platinum wire fused into *A*; *M* is a thin carbon rod, resting on the capillary portion of *C*, and connected with the wire *L*. There are cocks at *H* and *F*. *O* is an electromagnet, connected with the wires *L* and *N*. *Q* is a plunger held up by a spring in the piston, so that

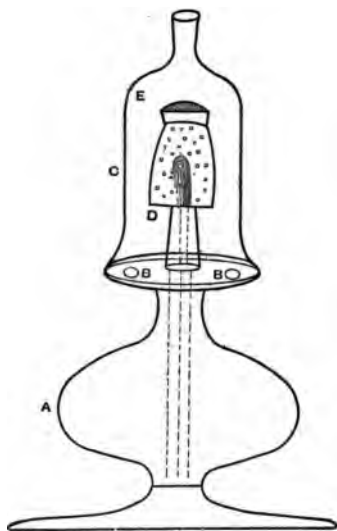


the gas can freely pass through the opening *R* to the burners as long as the magnet is not acting. When cocks *H* and *F* are open, and *G* and *D* are shut, the apparatus may be used as a simple air thermometer, and readings are taken on the tube *B*. To use it as a thermostat, the bath is raised to the required temperature, *G* and *D* are opened, and the mercury is adjusted until it nearly touches the carbon rod *M*, when *G*, *H* and *F* are then closed. If the temperature rises ever so slightly, the mercury will touch *M*, and the current from the battery *Z*, flowing through the wires *L* and *N*, will pull down the armature *P*, driving the cylinder *Q* down, and shutting off the gas, except what is necessary to keep the burners lighted. The apparatus is said to maintain a temperature constant within half a degree for days, and to work with any kind or pressure of gas, and only to require one cell to keep it going for months.

A. H. W.

**A New Appliance for the Detection of Combustible Gases when in Admixture with the Atmosphere.**—H. N. Warren, Chem. News 61, 279.

*A* is the reservoir of the lamp, containing petroleum spirit, surrounded by a gallery which is pierced with two holes *BB*. *D* is a copper thimble perforated with numerous small holes, and contains a coil of platinized asbestos *E*, in close proximity. The wick of the lamp is also of platinized asbestos made by saturating the finest quality of asbestos yarn in a strong solution of platonic oxalate (prepared by dissolving the hydrate of the metal in oxalic acid), drying, and igniting the residue in a porcelain crucible. To use the apparatus, the lamp wick is first lighted, and after the end of the wick becomes red-hot, the copper thimble *D* is placed over the wick, extinguishing the flame, but there will remain a glow. The glass chimney *C* is now put on, and samples the atmosphere

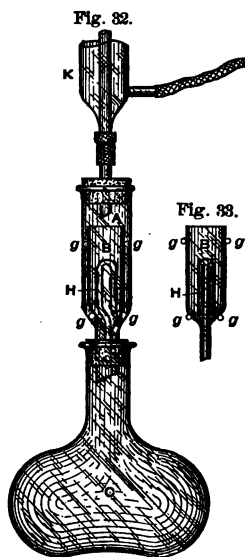


by causing an upward draught. If the air contains coal-gas or other hydrocarbons, the heated coil *E* will show their presence by becoming quickly incandescent. 0.5 per cent. by volume of combustible gases in the atmosphere may be detected by this apparatus.

A. H. W.

**New Extraction Apparatus.**—Dr. O. Knöfler, *Ztschr. anal. Chem.* **28**, 671.

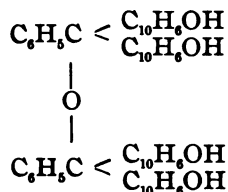
The apparatus shown in the annexed cuts is described as follows by the author: It consists of two cylindrical vessels *A* and *B*, placed one inside the other. The vessel *B* has some small knobs of glass, *gg*, fused on the outside, which serve to steady it while keeping the outside walls from coming in contact with the inside walls of *A*. The vessel *A* narrows at the lower end, and is closely fitted, either by a stopper or by grinding into the neck of the flask *C*, which contains the extraction liquid. *A* is closed at the upper end by a stopper, through which runs the tube of the condenser *K*. The vessel *B* serves to hold the material to be extracted; it is open at the top, and contains the U-shaped siphon tube *H*, the longer limb of which is fused into the lower end of *B*, reaching down into the narrowed part of *A*. The shorter leg reaches to the bottom of *B*. Fill *B* to a little below the bend of the siphon *H* with the material to be extracted, after putting a little cotton in the bottom to keep the siphon from being choked, and heat the liquid in *C* to the boiling point. The steam passes through the space between *A* and *B*, and condensing, flows into *B*, when it is kept almost at the boiling point by the steam passing around it. When *B* is filled above the bend of the siphon *H*, the liquid is drawn out, and runs down again into *C*, this operation continuing indefinitely as long as the liquid in *C* is boiled. The author claims that his apparatus has the advantages over Soxhlet's, that the extraction takes place at the ordinary pressure at the boiling point of the liquid, that it is less likely to



break, and much cheaper. Instead of the U-shaped siphon shown in Fig. 1, the form shown in Fig. 2, suggested by Bössenick (*Ztschr. anal. Chem.* **27**, 388) may be used. This apparatus works best with such liquids as alcohol, benzene, etc. A. A. B.

**A New Indicator, "a Naphtol-Benzoin."**—R. Zaloziecke, *Chem. Zeit.* **14**, 605.

This compound has also been prepared by Doebner,\* who gives it the following formula :



His method of preparation has been slightly modified by the author. 2 mol. a-naphtol and 1 mol. benzenetrichloride are diluted with benzene and allowed to stand 24 hours in a flask. The reaction is ended by heating to 30° or 40°, after which the excess of benzene and benzene trichloride are distilled off. The residue is purified by dissolving in a solution of caustic soda, and separating the compound by fractional precipitation with hydrochloric acid and washing this precipitate thoroughly with water. The pure salt is a reddish brown powder, which turns a bright green in presence of alkalis and an orange yellow in presence of acids. For analysis, 10–20 drops of a 1 per cent. alcoholic solution are used. 1 drop of  $\frac{n}{10}$  acid will produce a permanent change of color in a neutral solution. The author classes this compound with the phenolphthaleins, and finds it may be used with satisfactory results in every case except for carbonates, to which acid it gives the basicity of one. S. C.

**A Simple Form of Quick Filter.**—Joseph Torrey, *Chem. News* **61**, 292.

A platinum disk, one inch in diameter, is cut from ordinary stout foil, and pierced with small holes with a steel point, a margin of one-sixteenth inch being left unpierced. The disc is now placed in a funnel, which may be cut off if desired, so that the

\**Ann. der Chem.* **257**, 56; *Ber.* **12**, 1462.

disc is about  $\frac{1}{4}$  inch below the rim of the funnel. A round piece of filter paper, about one-sixteenth inch larger in diameter than the disc, is now placed in the funnel just above the disc. When water is applied, and pressure turned on, the paper settles down and makes an air-tight joint at the edge of the disc, when the precipitate can be brought on the paper and washed as usual.

A. H. W.

**Some Observations on Precipitation.**—George Watson, Chem. News 61, 207.

The author of this paper has made a study of precipitates, formed on the sides of beakers, where there has been a slight scratch, while the rest of the surface of the glass remained uncoated. He concludes that the fact is due not only to the increased potent surface-energy of the glass by abrasion, but also to a condensation change in the precipitate itself.

A. H. W.

**Correction in Thermometer Readings for the Part of the Stem Outside the Vapor.**—E. Reinbach (Ber. 22, 3070).

**Qualitative Tests for the Limit of Impurity in Chemicals of the U. S. Pharmacopœia.**—R. B. Warder, Am. Drug. 19, 82.

The author criticises some of the qualitative tests in regard to the distinction between cloudiness, turbidity, and precipitate, as prescribed by the U. S. Pharmacopœia, for detecting sulphates, chlorides, nitrates, and other impurities in certain chemicals. He proposes to use a dilute standard solution, reacting like the impurity to be tested, and then make a direct comparison of the two solutions in test tubes of equal size, so as to allow a careful judgment of the relative intensity of the two reactions.

*Solution to be Tested.*—This shall contain not less than 1 per cent. (or 1 gm. per 100 cc.) of the solid substance to be tested. Fluids may be diluted to 5 volumes. Strong acids may be partly neutralized, and salts may be acidified previous to such dilution.

*Quantity of Reagent Used.*—Test solutions may be added amounting to one-tenth the volume to be tested.

*Definition of Precipitate.*—Any perceptible cloudiness or opalescence appearing within ten minutes after the addition of the test solution, when examined in good light, will be regarded as a pre-

precipitate. The test solutions are made by dissolving 1 part of the solid in 10 or 20 parts of the solvent. The dilute standard solutions are prepared by taking 1, 2 or 3 cc. of test solution and diluting to one liter.

F. R. B.

**A System of Chemical Reagents, Based on the Equivalents of the Elements.**—Joseph Reddrop, *Chem. News* 61, 245, 256.

An equivalent reagent is defined as one which contains a milligramme equivalent of reacting substance in 1 cc. of solution, or a gramme equivalent to one liter. A solution of this strength is called an equivalent solution or an equivalent reagent, and is denoted by the symbol *E*. Thus, *E* sodium carbonate represents a solution containing 53 mg. in 1 cc., or 53 gms. in 1 liter. This, it will be noticed, is not a percentage solution, but one containing parts by weight (mgms.) of substance in parts by volume (cc.) of solution. The strength of all the reagents are expressed in terms of *E*. Thus, the strength of sulphuric acid, sp. gr. 1.84, is approximately 36 *E*. Where the substance is not sufficiently soluble to make an *E* solution, some fractional part is taken, *e. g.*,  $\frac{E}{2}$  hydrogen sulphide,  $\frac{E}{20}$  calcium oxide,  $\frac{E}{30}$  calcium sulphate,  $\frac{E}{600}$  strontium sulphate (test for barium). The fractional part may be also expressed decimally, if preferred. All *E* reagents are equal in precipitating or quantitative reacting power. If, for example, it takes 36 cc. of *E* sulphuric acid to exactly precipitate the lead as sulphate in a solution of that metal (not allowing for free sulphuric acid in excess), it will require the same number of cc. of *E* ammonium carbonate to precipitate the lead as carbonate, or of *E* potassium chromate to precipitate the lead as chromate. But 1 cc. of 36 *E* sulphuric acid, or 7.2 cc. of 5 *E* ammonium carbonate would also precipitate the same quantity of lead, but it would require at least 144 cc. of  $\frac{E}{4}$  hydrogen sulphide to precipitate the metal as sulphide. Variations of from  $\frac{1}{100}$  to  $\frac{1}{20}$  part in strength are permissible in making up *E* reagents, consequently they may be prepared in almost the same time as those which ordinarily fill the reagent bottles. Where reagents are expensive, an  $\frac{E}{5}$  or  $\frac{E}{10}$  solution may be used for qualitative work. 5 *E* is frequently employed in the case of reagents, as acids, where a

stronger solution than  $E$  is found necessary. When a reagent becomes weaker on standing, as sulphurous acid, the fact is indicated by placing a minus sign on the label of the bottle, thus,  $-4 E$  sulphurous acid. If there is an increase of strength, the symbol  $+$  is used, as  $E +$  stannous chloride. For the practical application of these multiple and fractional reagents, bromine and chlorine (Chem. Reagents No. 2) will serve as examples. Pure bromine is  $37 E$ . A saturated aqueous solution is  $\frac{E}{2}$ , and a saturated solution of chlorine in water is  $\frac{E}{5}$ . Now if 1 cc. of liquid bromine ( $37 E$ ) is needed to accomplish a definite amount of oxidation, it will require 74 cc. of  $\frac{E}{2}$  bromine water, or 185 cc. of  $\frac{E}{5}$  chlorine water to effect the same quantitative result. A few reagents require a double index of their strength, *e. g.*,  $E$  or  $\frac{2E}{3}$  hydrogen disodium phosphate, for this reagent behaves as an  $E$  solution when precipitating iron as phosphate, but as only  $\frac{2E}{3}$  when used to precipitate magnesium as ammonium magnesium phosphate, owing to the part ammonium plays in the latter reaction.

The advantages of this system are stated as follows :

1. It affords the most convenient method of expressing the proportionate strength or precipitating power of each reagent and one which may be plainly indicated on each bottle.

2. It indicates as near as can be practically attained, the actual strength of each reagent. Thus,  $36 E$  sulphuric acid contains 36 mgms., equivalents in 1 cc., and the equivalent of sulphuric acid being 40, there are  $40 \times 36 = 1764$  mg. = 1.765 gms. sulphuric acid present in 1 cc., and similarly each cc. contains  $1 \times 36 = 36$  mgms. = 0.036 gm. hydrogen ;  $16 \times 36 = 0.576$  gm. sulphur, and  $32 \times 36 = 1.152$  gms. of oxygen.

3. By observing the quantity of a reagent employed in an analysis, we can calculate the quantity of by-product therefrom, and decide from that as to the amount of the dilution of our solutions.

4. In qualitative analysis, we can form a better judgment of the amount of the substance present.

5. The strength of reagents may be most conveniently expressed in this system, for example :

Nitric acid, sp. gr. 1.4268 at  $15.5^{\circ}$  C. is exactly  $16 E$  in strength.

"	"	1.1656	"	"	"	5 $E$	"
"	"	1.0456	"	"	"	$E$	"

which gives a more accurate idea of the strength than the specific gravity.

6. Reagents may be most readily diluted to the various strengths required in analysis.

7. This system affords the simplest method of calculating the theoretical quantity of reagent required to effect any chemical change.

8. It also affords a simple method of calculating the quantity of gas given off in chemical reactions.

9. It offers the most convenient method for expressing the precise acidity, etc., of chemical solutions intended for accurate titration, precipitation, etc. For example, in Marguerite's volumetric method for iron, by means of  $\frac{n}{10}$  potassium permanganate, it is recommended that the solution for titration be acidified to  $E$  or  $\frac{E}{2}$  sulphuric acid, thus expressing the acidity at which the reaction should take place. As illustrating the application of the method to precipitation, it is mentioned that lead precipitated as sulphate is lead soluble in  $E$  sulphuric acid. Comprehensive tables accompany the article.

A. H. W.

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## INORGANIC ANALYSIS.

**The Volumetric Analysis of Copper.**—Reginald A. Fessenden, Chem. News 61, 183.

Several experiments having demonstrated the hopelessness of expecting accuracy when ammonia was used to neutralize copper solutions, before titration with potassium cyanide, the author tried sodium carbonate as a neutralizer, and found it to answer admirably well.

A. H. W.

**The Estimation and Separation of Tellurium.**—E. Donath, Ztschr. angew. Chem., 1890, 214.

3 or 4 gms. of the finely ground substance are placed in a porcelain dish, and nitric acid added. When oxidation is complete, the excess of acid is evaporated, care being taken not to raise the heat too high. The contents of the dish, after being dried, are rubbed with an agate pestle while soda solution is added. The combination of the acid and alkali will cause considerable heat to



be evolved, and any copper that may be in the substance will cause a black color to appear at this point. After digesting for one-half hour more, soda solution is added, and an equivalent amount of water, the solution filtered, and the filtrate boiled for about twenty minutes with pure grape sugar, when the tellurium is completely precipitated, and can be taken as such or calculated to telluric acid.

J. E. W.

**The Rapid Estimation of Arsenic.**—F. W. Boam, Chem. News **61**, 219.

The author uses the following modification of the "uranium acetate method:" 1 to 1.5 gms. of the powdered ore, dried at  $100^{\circ}$ , is taken and evaporated to dryness with 20 to 25 cc. conc.  $\text{HNO}_3$ . When cool, 30 cc. strong  $\text{NaOH}$  solution (30 per cent) are added and boiled for a short time, when the liquid is filtered and diluted to 250 cc. 25 cc. of this solution is acidulated with a ten per cent. solution of sodium acetate in 50 per cent. acetic acid, and the liquid is boiled. It is then titrated with a quarter normal solution of uranium acetate (17.1 gms. uranium acetate, dissolved in 15 cc. strong acetic acid, and diluted to 2 liters), 1 cc. of which is equivalent to 0.00025 gms. arsenic. A solution of  $\text{K}_2\text{FeCN}_6$  is used as the indicator, a drop of the test solution giving a reddish brownish coloration with this on a white tile, when the titration is finished. A sample of "arsenical iron pyrites" may be analyzed by this method in less than two hours. There is a tendency to form an unstable, arseniate of iron, on adding the sodium hydroxide solution, but this difficulty is overcome by employing a moderately strong solution of the hydroxide in excess, and boiling.

A. H. W.

**The Volumetric Analysis of Copper.**—Reginald Fessenden, Chem. News. **61**, 253.

Mr. Fessenden replies to the three objections urged against the use of a sodium carbonate solution in titrating with potassium cyanide, as follows:

(1) "That sodium carbonate does not dissolve, but precipitates copper." When free nitric acid is present, solution is effected, but sodium bicarbonate does not give a solution under the same conditions.

(2) "That a large quantity is necessary to effect solution." But 20 to 30 cc. is amply sufficient for any ordinary analysis, and the increased accuracy of the method permits the use of small quantities of ore for determinations.

(3) "That the amount of sodium carbonate in the solution affects the amount of potassium cyanide used." To one of two copper solutions of equal strength and volume, and containing equal amounts of free nitro-sulphuric acid, was added 20 cc. of a saturated solution of sodium carbonate, just sufficient to redissolve the precipitated copper. To the other was added 250 cc. of the same sodium carbonate solution. On titration, the amount of KCN used for each was identical. It is true, however, that the use of sodium hydroxide (or sodium carbonate in absence of free acid) does cause the amount of KCN required to vary greatly. This is due to the fact that a precipitate having a large molecular weight separates out when NaOH is added in slight excess. As more alkali is added, the precipitate becomes more simple and more stable, and therefore less acted upon by the KCN, but the case is different when the alkali added forms a solution. The above reaction may also be applied to the volumetric estimation of nickel.

A. H. W.

**The Volumetric Determination of Free Halogens, and the Determination of Iodides in Presence of Chlorine and Bromine.**—P. Lebeau, Chem. News 61, 163 (Comptes Rendus 110, 520).

Into a 200 cc. flask are put 30 or 40 cc. of carbon disulphide, and as much distilled water, and then a known quantity of the iodized solution to be examined. After adding a few drops of indigo extract, standard bromine is then dropped in from a burette with a glass top, stirring briskly. The iodine is set free, is dissolved in the carbon disulphide, which turns violet, while the supernatant liquid remains blue, until a bromine water in excess decolorizes the extract of indigo. Before each series of analyses, the relative value of the bromine water must be determined by means of potassium iodide of known strength. The author found the value of the bromine water in his determinations in an independent manner, without employing an iodide. He found it convenient to convert the free halogens into the corresponding zinc

salts, and then to titrate with a standard solution of silver. The liquid containing the free halogen is put into a stoppered flask, and a few gms. of pure zinc powder are added. Almost immediately the halogen disappears, and, in the case of bromine, neutral zinc bromide is formed, which may be titrated with a standard silver solution, using neutral potassium chromate as an indicator.

A. H. W.

**On Some Applications of Caustic Soda or Potash and Carbon in the Qualitative and Quantitative Analysis of Minerals.**—Charles A. Burghardt, *Chem. News* **61**, 260. (From the "Memoirs and Proceedings of the Manchester Literary and Philosophical Society, Vol. 3, Fourth Series).

For the analysis of minerals, insoluble in acids, the author uses a fusion mixture consisting of finely divided charcoal, about 10 per cent. of the weight of the mineral, and introduces the mixture carefully into a silver crucible containing fused caustic soda or potash, about six times the weight of the mineral taken for analysis, when the crucible is heated over a Bunsen flame until the reaction is complete. Applying the above method to "black tin" from Cornwall, it was found that 95 per cent. of the total tin in the ore was taken up in the first fusion. In the analysis of wolframite, the iron is entirely separated from the tungstic acid at once. The tungstic acid is precipitated from the filtrate by adding a slight excess of hydrochloric acid and boiling, when the anhydride,  $WO_3$ , comes down as a yellow powder. The method was modified, in the case of chrome iron-ore, by the addition of ammonium nitrate (about three times the weight of the mineral taken) to the solid caustic soda before the latter is put into the crucible, in order to oxidize the chromic oxide liberated at once to chromic acid, when sodium chromate is formed. Rutile, ilmenite, and barytes were successfully examined qualitatively by this method. Whether it is applicable for minerals where sulphur, arsenic, or antimony enter largely into their composition, is a question with which the author is now occupied.

A. H. W.

**Determination of Potash and Humus in Soils.**—J. Raulin, *Chem. News* **61**, 154 (*Comptes Rendus* **110**, 289).

The author's method depends upon the very slight solubility of

potassium phosphomolybdate in aqueous liquids, since the phosphomolybdate weighed is nineteen times as heavy as the potash to be determined, a relatively small sample of the soil may be taken for analysis. The phosphomolybdic reagent is prepared as follows: 100 gms. pure crystalline ammonium molybdate is dissolved in a minimum of water, and 6.5 gms. neutral crystalline ammonium phosphate, previously dissolved in a little water, is then added. Ammonium phospho-molybdate is thrown down by aqua regia, and heat is applied until the precipitate redissolves. The solution is then evaporated to dryness, first over the flame, and finally on the water bath at about 70°. 400 cc. of water and 5 cc. of nitric acid are now added, when the whole is heated and filtered. The wash for the potassium phospho-molybdate is made by dissolving 20 gms. sodium nitrate in 1 liter of water, adding 2 cc. of nitric acid and 1.2 cc. of a solution of nitre (80 gms. to the liter) slightly heated to saturate the liquid with potassium phosphomolybdate. After stirring up and allowing to settle, the clear liquid is decanted. For analysis, a portion of the soil containing about 15 gms. of anhydrous potash is weighed out, the potassium salts are extracted by the usual means, and converted into nitrates, when the liquid is concentrated to a few cc. and slightly acidulated with nitric acid. 4 cc. of the phospho-molybdic reagent are added for every 10 mgms. of anhydrous potash supposed to be present, the solution is evaporated to dryness at 50°, filtered through very small counterpoised double filters, and the precipitate is washed with the washing solution. The counterpoise is washed with the same liquid, and the filters are dried at 50° and weighed.  $\text{Weight} \times \frac{5.2}{100} = \text{K}_2\text{O}$ .

For the determination of humus, the author has modified the method of J. H. Schmidt. The humic liquor is prepared by treating 10 gms. of the soil with soda, in the ordinary manner, and taking a fraction of the liquid. In a 250 cc. flat-bottomed flask are introduced 10 cc. of a solution of manganese sulphate (16 gms. anhydrous salt per liter) and 10 cc. of a solution of potassium permanganate (10 gms. per liter), and the mixture is heated until the "manganese bronze" is precipitated. After adding 100 cc. of water and 4 cc. of sulphuric acid (150 cc. of the monohydrated acid per liter), an exactly measured quantity of the

humic liquid is poured into the flask, a sufficient quantity, so that when completely oxidized, it may destroy at most half the manganese peroxide. The mixture is now boiled for eight hours, the water being renewed as it is driven off. The manganese peroxide not attacked is dissolved by heat in a small measured quantity of decinormal oxalic acid, and the excess of the latter is determined by titrating with potassium permanganate (1 gm. per liter). The volume of oxalic acid which destroys the same amount of peroxide as the humus is calculated by taking the difference between the volume of oxalic acid required to destroy all the peroxide formed by 10 cc. of permanganate solution (10 gms. per liter) and the volume required to destroy the peroxide after the action of the humus. The number of cc. of oxalic acid equivalent to the total volume of humic liquid may be readily determined, and consequently the volume of oxalic acid equivalent to the humus in 10 gms. of soil. This number of cc. multiplied by 0.8 mgms. will express in mgms. the weight of oxygen necessary to burn the humus of 10 gms. of dry soil.

A. H. W.

#### **Determination of Alkalies in Presence of Sulphates.—**

Jas. Grant and J. B. Cohen, J. Soc. Chem. Ind. 9, 19.

A measured volume of hydrogen peroxide is put into a beaker together with three or four drops of methyl orange. As hydrogen peroxide is always slightly acid, a small quantity of a very dilute solution ( $\frac{1}{100}$ ) of sodium hydroxide is added until the neutral point is reached. Next the required quantity of alkaline sulphite is added, and boiled up at once, but gently. During the latter part of the boiling the methyl orange is bleached. The solution is cooled, a few more drops of methyl orange added, and then titrated with normal hydrochloric acid solution. Both methyl orange and litmus give the same results, but the former shows the neutral point more distinctly. It was found by experiment that in caustic salts of commerce containing about 50 per cent. of sulphite, 10 cc. of commercial hydrogen peroxide for every gram of salt solution was sufficient. For salts containing above 50 per cent. of sulphite, it is better to take double the volume of hydrogen peroxide. It is unnecessary to let the mixture of alkaline sulphite solution and hydrogen peroxide stand half an hour before

boiling up, as the increase in quantity of acid required for neutralization is almost inappreciable.

O. O. I.

**Determination of Lithia in Mineral Waters.**—E. Waller, Jour. Am. Chem. Soc. 12, 214.

The author states that the three methods now practically available are, Mayer's modification of the phosphate method, Gooch's amyl alcohol method, and Carnot's fluoride method. Assuming that we have obtained a concentrated aqueous solution from a known quantity of water, containing all of the lithium and some of the potassium and sodium chlorides, but no other bases. The phosphate method is as follows: An excess of hydrodisodium phosphate is added, and then a slight excess of sodium hydrate, evaporating to dryness, redissolving in water by the aid of heat, adding an equal volume of strong ammonia, digesting, and warming for some time. Allow to stand twelve hours. Filter, wash with a mixture of equal parts of water and ammonia, dry, ignite, and weigh as  $\text{Li}_2\text{PO}_4$ . A second or third portion of precipitate may be recovered by evaporating the filtrate and washings, adding ammonia, and allowing to stand as before, filtering, etc. Gooch's method consists of adding to the concentrated solution of the alkaline chlorides containing about 0.2 gm. of salt, in all, 30 to 50 cc. of pure anhydrous amyl alcohol. This is then heated on the sand bath, and the water boiled off through the amyl alcohol. The heating is kept up until the volume of amyl alcohol has been reduced to 15 or 18 cc. After cooling, a few drops of hydrochloric acid are added, and the heating repeated for a short time. The amyl alcohol is filtered into a measuring cylinder, and its volume noted (10 to 15 cc.). The salts are then washed with cold amyl alcohol, and the washings and filtrate are evaporated in a weighed platinum dish. From this weight, for every 10 cc. of amyl alcohol which remained in contact with the chlorides after heating, the following deduction is made:

When only sodium and lithium chlorides were present,	0.00050 gm.
“ potassium “ “ “ “	0.00059 “
When both sodium and potassium, as well as lithium chloride, were present	0.00109 “

Carnot's fluoride method is as follows: The mixed alkaline chlorides, after evaporation nearly to dryness, are extracted with

a mixture of equal parts of alcohol (90 per cent.) and ether, and allowed to stand over night, then filtered through a small filter, and washed with alcohol. A second extraction may be necessary, the work being controlled by the indications of the spectroscope. The ether and alcohol are evaporated, and the salts dissolved in a little water, then filtered into a weighed platinum dish. The filtrate and washings should be concentrated to about 5 or 10 cc., ammonium fluoride and ammonia are then added, and the dish is set aside over night to allow the  $\text{LiF}$  to precipitate. The solution is filtered and washed several times by decantation with a mixture of 1 part of the reagent and 5 or 10 of ammonia. The bulk of the filtrate and washings (30 to 50 cc.) is noted, the filter paper and contents are placed in a weighed dish, sulphuric acid added, and heated until the paper has been incinerated, and the lithium converted into sulphate, cooled, and weighed. To this is added 0.0040 gm. for every 7 cc. of filtrate and washings, and the result estimated as  $\text{Li}_2\text{SO}_4$  and calculated to  $\text{Li}$ ,  $\text{LiHCO}_3$ . F. R. B.

**Estimation of Ammonia by Ruffle's Method.**—Alexander Buchan, Chem. News 61, 231.

The objection to Ruffle's method, viz., that the contents of the tube will fuse, and the subsequent cleaning is troublesome, is overcome by the use of soda-lime, prepared as follows: Quick-lime and washing soda are ground through a riddle of sixteen holes to the linear inch, mixed in equal proportions, and heated in an iron pot over an ordinary fire, constantly stirring, until no more water vapor is given off. The pot should not be more than one-third full, as the mixture swells greatly. This soda-lime, it is stated, will not fuse. A synthetical manure was made containing the amounts as below:

Parts.		Containing per cent. $\text{NH}_3$ .	
9	Dissolved Bone Manure . . . . .	1.25	$9 \times 1.25 = 11.2$
1	Belgian Phosphate . . . . .	—	—
$1\frac{1}{2}$	Fish Guano . . . . .	10.41	$1\frac{1}{2} \times 10.41 = 15.6$
$1\frac{1}{2}$	Liebig's Guano . . . . .	8.62	$1\frac{1}{2} \times 8.62 = 12.9$
4	Sulphate of Ammonia . . . . .	24.75	$4 \times 24.75 = 99.0$
3	Chloride of Potassium . . . . .	—	—
20			$20 \mid 138.7$
			6.93

0.8 parts of the above containing 7.00 per cent.  $\text{NH}_3$ — $0.8 \times 7.00 = 5.60$   
 0.2 " pure potas'm nitrate, " 16.83 " " — $0.2 \times 16.83 = 3.36$

**.8.96**

A. H. W.

The solution of permanganate was prepared by dissolving 5 gms. of the crystallized salt in a liter of distilled water, boiled for three hours, and when cold, diluted to one liter. The strength of the solution was determined by titration with iron wire dissolved in sulphuric acid, and also by solution of ferrous ammonium sulphate. One-half of the solution was exposed to the light, and the other kept in the dark, both in well-stoppered bottles. The testing was made, each time, with iron wire and ferrous ammonium sulphate. The results show that light has no influence in the change, but that regular, though slight, decrease in strength occurs.

Strength of 1 cc. $\text{KMnO}_4$ in gms. of Iron.			Strength of 1 cc. $\text{KMnO}_4$ in gms. of Iron.		
DATE.	Exposed to Light.		DATE.	Kept in the Dark.	
	Iron Wire.	Double Salt.		Iron Wire.	Double Salt.
1887.			1887.		
Nov. 14 . . . .	.00968	. . .	Nov. 14 . . . .	.00968	. . .
Dec. 1 . . . .	.00964	.00963	Dec. 1 . . . .	.00964	.00963
" 10 . . . .	.00960	.00960	" 10 . . . .	.00963	.00960
20 . . . .	.00961	.00959	" 20 . . . .	.00959	.00962
1888.			1888.		
Jan. 10 . . . .	.00955	.00959	Jan. 10 . . . .	.00959	.00959
Mar. 8 . . . .	.00940	.00941	Mar. 8 . . . .	.00948	.00952

O. O. L.



**Determination of Chlorine and Hydrochloric Acid in a Mixture of the Two Gases.**—W. Younger, J. Soc. Chem. Ind. 8, 88.

A glass tube, 20 inches long by  $\frac{7}{8}$  inch in diameter, is employed for absorbing the gases. This tube is corked, and through the cork two other tubes are passed, one reaching the bottom and the other merely passing through the cork. Over the end of the longer is tied a piece of thin cotton cloth, which serves to break up the gas bubbles as they pass from the lower end of this tube. Two pieces of copper wire are also twisted around the lower end of the long tube, the four ends of which are allowed to project, so as to keep it in the middle of the absorbing tube. Into the absorbing tube are put 100 cc. of a standard solution of arsenious acid in water, every cc. of which equals 0.15432 of a grain of chlorine, and to which is also added a very small portion of sulphate of indigo paste, which serves to indicate when the aspiration is finished. Absorb the gases completely in the solution. Next to the absorbing tube is placed a bottle, containing a solution of potassium iodide and water, which also serves as an indicator. This bottle is in turn coupled up to a graduated box, fitted up as an aspirator. This aspirator is provided with a gauge-glass, down the one side of which are the readings for the grains chlorine per cubic foot, while down the other side on the same lines are the number of cc. drawn through, the latter being required in order to obtain the grains of hydrochloric acid. In taking an aspiration, the indication appears first in the iodide of potassium bottle by the liberation of iodine, and shortly afterwards the sulphate of indigo becomes bleached. At this point the aspiration is stopped, and the readings taken.

Suppose the level of the water in the gauge-glass stood at the point marking one cubic foot when the aspiration was finished, then the grains chlorine per cubic foot would be exactly 15.432. If finished when half a cubic foot had been drawn through, then it would indicate twice the quantity of chlorine. From the same aspiration is also obtained the grains hydrochloric acid. After taking an aspiration, 10 cc. of the solution from the absorbing tube are titrated with decinormal silver. If no hydrochloric acid is present in the gases, then 28.2 cc. of silver will be required,

being equal to the hydrochloric acid produced by the oxidation of the arsenious acid. Any silver solution required beyond 28.2 cc. is due to hydrochloric acid in the gases, which is calculated into grains per cubic foot by reading off the number of cc. drawn through.

O. O. L.

**Conversion Table for Fehling's Solution.**—E. Wein, Chem. Zeit. Rep. 14, 106.

A soda solution is made by dissolving 517 gms. sodium hydrate in 1 liter of water. 100 cc. of this solution are added to a solution of 273 gms. in 400 cc. water. A copper solution is made by dissolving 69.278 gms. copper sulphate in 1 liter of water. The following precautions are necessary: 1. The Fehling solution must be used undiluted. 2. 30 cc. of the copper solution and 30 cc. of the solution must be mixed only a short time before using. 3. The sugar solution must not contain more than 1 per cent. of sugar. If such is the case, it must be diluted so that the 60 cc. of Fehling's solution will not be used for more than 25 cc. of 1 per cent. sugar solution. 4. The mixture of these solutions must not be heated longer than two minutes. 5. The final solution must be filtered through asbestos, and not through paper. The table is given as follows:

Copper. mg.	Sugar. mg.
10 . . . . .	4.5
15 . . . . .	7.0
20 . . . . .	9.5
25 . . . . .	12.0
30 . . . . .	14.6
35 . . . . .	17.1
40 . . . . .	17.6
45 . . . . .	22.1
50 . . . . .	24.6
55 . . . . .	27.2
60 . . . . .	29.7
65 . . . . .	32.2
70 . . . . .	34.7
75 . . . . .	37.3
80 . . . . .	39.8
85 . . . . .	42.3
90 . . . . .	44.8
95 . . . . .	47.4

Copper. mg.	Sugar. mg.
100 . . . . .	49.9
105 . . . . .	52.4
110 . . . . .	54.9
115 . . . . .	57.5
120 . . . . .	60.0
125 . . . . .	62.5
130 . . . . .	65.1
135 . . . . .	67.7
140 . . . . .	70.3
145 . . . . .	73.9
150 . . . . .	75.5
155 . . . . .	78.2
160 . . . . .	80.8
165 . . . . .	83.4
170 . . . . .	86.0
175 . . . . .	88.6
180 . . . . .	91.2
185 . . . . .	93.8
190 . . . . .	96.4
195 . . . . .	99.1
200 . . . . .	101.7
205 . . . . .	104.4
210 . . . . .	107.0
215 . . . . .	109.7
220 . . . . .	112.3
225 . . . . .	115.0
230 . . . . .	117.6
235 . . . . .	120.2
240 . . . . .	122.9
245 . . . . .	125.5
250 . . . . .	128.3
255 . . . . .	131.1
260 . . . . .	133.7
265 . . . . .	136.4
270 . . . . .	139.1
275 . . . . .	141.9
280 . . . . .	144.6
285 . . . . .	147.3
290 . . . . .	150.0
295 . . . . .	152.8
300 . . . . .	155.6
305 . . . . .	158.3
310 . . . . .	161.1
315 . . . . .	163.9

Copper. mg.	Sugar. mg.
320 . . . . .	166.7
325 . . . . .	169.4
330 . . . . .	172.2
335 . . . . .	175.0
340 . . . . .	177.8
345 . . . . .	180.6
350 . . . . .	183.3
355 . . . . .	186.1
360 . . . . .	188.9
365 . . . . .	191.8
370 . . . . .	194.7
375 . . . . .	197.6
380 . . . . .	200.5
385 . . . . .	203.4
390 . . . . .	206.3
395 . . . . .	209.1
400 . . . . .	212.0
405 . . . . .	214.9
410 . . . . .	217.8
415 . . . . .	220.7
420 . . . . .	223.6
425 . . . . .	226.5
430 . . . . .	229.4
435 . . . . .	232.4
440 . . . . .	235.3
445 . . . . .	237.6
450 . . . . .	240.6
455 . . . . .	243.5
460 . . . . .	246.5
465 . . . . .	249.4
470 . . . . .	252.4

**The Separation and Determination of Zinc in Presence of Iron and Manganese.**—J. Riban, Chem. News **61**, 307, (Comptes Rendus **110**, 1196).

For the direct determination of zinc in presence of iron (ferrous or ferric) or manganese, the solution is diluted so that it contains about 0.1 gm. in 100 cc., when it is saturated with sodium carbonate until a slight permanent precipitate forms, which is dissolved in a few drops of dilute hydrochloric acid. Sulphuretted hydrogen is now passed into the cold liquid, when most of the

zinc is precipitated, together with sulphur from the reduction of the ferric salt. A large excess of a solution of sodium hyposulphite is now added, and the current of sulphuretted hydrogen continued, when the last traces of zinc are precipitated, while the iron remains in solution. Ammonium hyposulphite is recommended for the subsequent precipitation of ferric oxide, when the determination of the iron is required, and ammonia or ammonium carbonate is used to neutralize the free acid at first. The precipitate of zinc sulphide is dense, and collects readily. It is allowed to stand for five or six hours at least, when it is washed by decantation in water containing sulphuretted hydrogen, and filtered, when it often takes a slightly violet tint. The precipitate is now ignited with sulphur in a current of hydrogen (H. Rose's apparatus), and weighed. It is freed from traces of iron by dissolving the contents of the crucible in hydrochloric acid, adding a few drops of nitric to peroxidize the iron, and supersaturating with ammonia, after the addition of a large excess of ammonium chloride to prevent the precipitation of the zinc, and the weight of the zinc sulphide is corrected in accordance with the weight of the iron found. If the iron in the liquids freed from zinc is required, it may be determined by concentrating the solutions, oxidizing with nitric acid, and precipitating with ammonia. The same method is applicable in the separation of zinc from manganese, zinc sulphide carrying down only slight traces of manganese. In the case of ores containing lead, that metal must be first separated.

A. H. W.

**Determination of Cadmium as Sulphide.**—W. Minor, *Chem. Zeit.* **14**, 439.

After further experimenting in this line,\* the author finds that the cadmium may be weighed as a sulphide. The material for analysis is dissolved in nitric or hydrochloric acid, and the lead is precipitated as a sulphate with sulphuric acid. The filtered solution is then treated with an excess of sodium hydroxide, which precipitates the cadmium and iron. This precipitate is treated with ammonia, and the undissolved hydroxide of iron is filtered off and washed. The cadmium in the filtrate is precipitated with

\*This Journal **4**, 80, 213.

sodium sulphide solution, and filtered on a weighed filter, washed, and dried at  $140^{\circ}$ . This will give a hard mass having a constant weight. S. C.

## ATOMIC WEIGHTS.

EDITED BY F. W. CLARKE.

**Magnesium.**—Burton and Voree convert pure distilled magnesium by treatment with nitric acid and subsequent ignition into oxide.

0.33009 gm. Mg	gave	0.54766	MgO
0.34512	" "	0.57252	" "
0.26058	" "	0.43221	" "
0.28600	" "	0.47432	" "
0.30917	" "	0.51273	" "
0.27636	" "	0.45853	" "
0.36457	" "	0.60475	" "
0.32411	" "	0.53746	" "
0.32108	" "	0.53263	" "
0.28323	" "	0.46988	" "

From these data, which are closely concordant,

$$\begin{aligned} \text{If O} &= 16, \\ \text{Mg} &= 24.287. \end{aligned}$$

—*Am. Chem. Journ.* **12**, 219.

**Lanthanum.**—The atom weight of this element was redetermined by the usual method, viz., the conversion of the oxide into the sulphate.

0.9146 gm. $\text{La}_2\text{O}_3$	gave	1.5900	$\text{La}_2(\text{SO}_4)_3$
0.9395	" "	1.6332	" "
0.9190	" "	1.5877	" "
1.0651	" "	1.8515	" "

In these, the percentage of oxide in the sulphate ranges from 57.522 to 57.526.

$$\begin{aligned} \text{If O} &= 15.96 \text{ and S} = 31.98, \\ \text{La} &= 138.28. \end{aligned}$$

This is practically identical with the value found by Brauner and by Cleve.—*Ann. d. Chem.*, **256**, 168.

**Indium.**—Redetermined by Joly, from experiments upon the sesquihaloid salts. The salt  $\text{IrCl}_3, 3\text{KCl}, 3\text{H}_2\text{O}$ , dried at  $120^\circ$  and reduced in hydrogen, gave, in percentages :

36.872	Ir and	42.652	KCl.
36.842	"	42.720	"
36.873	"	42.742	"
Mean, 36.862		42.705	

From the ratio between Ir and KCl,

$$\begin{aligned} \text{when } \text{H}=1 \text{ and } 3\text{KCl}=223.224, \\ \text{Ir}=192.68. \end{aligned}$$

The dry ammonium salt,  $\text{IrCl}_3, 3\text{NH}_4\text{Cl}$ , treated similarly, gave

42.017	Ir
41.990	
Mean, 42.003	

$$\begin{aligned} \text{Hence, if } 3\text{NH}_4\text{Cl}+3\text{Cl}=266.24, \\ \text{Ir}=192.82. \end{aligned}$$

—*Compt. Rend.* 110, 1131.

**Bismuth.**—Classen converts the pure electrolytical metal into  $\text{Bi}_2\text{O}_3$ , by oxidation with nitric acid. The percentages of oxygen in  $\text{Bi}_2\text{O}_3$ , appear in the third column.

25.0667	gm. Bi gave	27.9442	$\text{Bi}_2\text{O}_3$	10.297
21.0691	"	23.4875	"	10.2965
27.2596	"	30.3922	"	10.307
36.5195	"	40.7131	"	10.300
27.9214	"	31.1295	"	10.3056
32.1188	"	35.8103	"	10.308
30.1000	"	33.5587	"	10.306
26.4825	"	29.5257	"	10.307
19.8008	"	22.0758	"	10.305

Mean, 10.304

If  $\text{O}=16$ ,  $\text{Bi}=208.923$ . In vacuo, 208.902.

If  $\text{O}=15.96$ ,  $\text{Bi}=208.401$ . In vacuo, 208.380.

—*Berichte* 23, 938.

## IRON AND STEEL.

EDITED BY P. W. SHIMER.

**Wiborgh's Method for the Analysis of Sulphur in Iron and Steel.**—J. B. Cohen, *J. Soc. Chem. Ind.* **9**, 16.

The apparatus consists of a wide-necked flask of 250–300 cc. capacity, to which is fitted a double-bored cork. Through one hole passes a tap-funnel, which terminates just below the cork, and through the other a cylindrical glass tube about 21 cm. long, open at both ends. The upper end of the glass tube is about 6 cm. in diameter, and the lower end drawn out so as to pass through the second hole in the cork. The amount of sulphur is determined by the depth of the yellow stain produced by sulphuretted hydrogen on the surface of a piece of calico previously soaked in a 5 per cent. cadmium acetate solution, and dried, the calico being stretched across the wide open end of the cylindrical tube. After half filling the flask with water, boil to expel the air, quickly introduce the sample of iron or steel, and boil again for a few minutes. Then add dilute sulphuric acid (1 in 5) through the tap funnel. This must be done gradually, so as not to interrupt the heating. When the iron is completely dissolved, boil about 10 minutes. Remove the calico, rinse well, and dry, and compare the stain with a set of standard colors. The set of standards (six shades is sufficient) is prepared by taking a sample of iron containing a known quantity of sulphur, and obtaining various shades with different weights of the sample by the method described above. The weight of sulphur is determined by the following formula :

If  $w$  is the weight of the standard sample corresponding to the standard shade containing  $s$  of sulphur, and  $w$  is the weight of the sample taken, then the weight of sulphur  $s$ , in the sample is

$$s = \frac{ws}{w}$$

O. O. L.

**The Use of Nitroso B-Naphthol for the Determination of Iron and for its Separation from Manganese and Aluminium.**—L. L. DeKoninck, *Chem. News* **62**, 19, (*Revue des Mines* **9**, 243).



Meinecke uses the new reagent as follows in the determination of iron. To the solution, free from nitrate, and containing the iron as much as possible as chloride or sulphate, ammonium carbonate is added until a slight permanent precipitate forms, which is dissolved by one drop of hydrochloric acid. A solution of nitroso-*beta*-naphthol in an equal weight of 50 per cent. acetic acid is now poured into the liquid, drop by drop, and there should be at least 10 parts of the reagent to one of iron. It is best to peroxidize the iron with bromine or potassium chlorate before the precipitation, since the ferric naphtholate is more readily washed than the ferrous. If a drop of the liquid, which has become clear on standing, produces a reddish-brown precipitate with a drop of cobaltous solution, the precipitation is complete. The precipitation is best conducted in the cold to avoid the precipitation of a basic salt of aluminum. The precipitate is washed until the washings leave no residue on platinum foil, dried until it can be removed from the funnel without tearing the filter, when it is put into a weighed porcelain crucible. Heat is applied to the covered crucible, gradually, until detonations cease, then the temperature is raised, and the residue is ignited, uncovered, and weighed as ferric oxide. Von Knorre advises that not more than 0.3 gm. be taken for an analysis. Copper and cobalt are also carried down, and phosphorus wholly or in part, and the phosphorus is found entirely in the precipitate if ammonium acetate is added to the neutralized ferric solution before precipitating. The ferric precipitate is completely free from manganese by this method. For the separation of iron and aluminum, Von Knorre pours an acetic acid solution of naphthol at one-twentieth into the metallic solution containing a notable excess of acetic acid. Meinecke uses a slightly acid solution and a concentrated solution of the reagent as above. The filtrate from the iron is evaporated to expel the excess of acetic acid, and the alumina is precipitated by ammonia. If much manganese is present, it is better to separate the iron and manganese from the other metals by the ordinary methods, and to use the naphthol reagent only for the separation of iron and aluminum. The presence of this reagent does not interfere with the subsequent determination of the calcium and magnesium by the usual methods.

A. H. W.

**A Rapid Method for the Determination of Aluminum in Iron and Steel.**—Chem. News 61, 313.

Take 10 gms. of the iron or steel, dissolve in a mixture of 50 cc. concentrated HCl and 30 cc. of water in a No. 8 beaker, and after solution, add 5 cc. of a saturated solution of sodium phosphate, then 100 cc. of water. Neutralize the free acids with dilute ammonia, and add dilute HCl until the solution becomes clear, then 2 cc. (not more) of conc. HCl, and boil. While boiling, pour in 50 cc. of a saturated solution of sodium hyposulphite, cover, and keep boiling one hour. Filter, wash with hot water, wash residue afterward into the same beaker in which it was boiled, dissolve in 100 cc. of a 10 per cent. solution of HCl, boil, and filter off the sulphur. Evaporate filtrate to 5 cc., wash into a platinum dish, neutralize with pure sodium hydrate (prepared from sodium), add 2 gms. sodium hydrate in excess, boil for half an hour, dilute, filter off the iron, and acidulate the filtrate with HCl. Precipitate the aluminum with ammonia, boil, filter off the aluminum phosphate, dissolve in a small quantity of HCl, and evaporate to dryness, to separate silica. Redissolve in HCl, filter, to the filtrate add 5 cc. of ammonium phosphate, then ammonia with a few drops of ammonium acetate, and boil for half an hour. Filter, and wash residue well with hot water containing a little ammonium phosphate, ignite, and weigh as  $\text{AlPO}_4$ , which contains 22.358 per cent. aluminum. It is said the above process can be easily executed in six hours.

A. H. W.

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ORGANIC ANALYSIS.**Milk Analysis.**—Francis Walls, Chem. News 61, 162.

The author describes his method as a modification of the "Adams" process. In place of the blotting paper coil, a tube containing asbestos is used. A test tube 18 to 20 mm. wide with the bottom cut off, leaving a tube about 80 or 90 mm. long, is packed with long fiber ignited asbestos, in the middle portion, about one-third the length of the tube. After weighing the tube, 5 cc. of milk are run on the asbestos, the tube is then weighed, and afterward placed on a water-jacketed drying oven, and heated to 100° C. An aspirator tube passes into the oven, by means of

which a steady current of air is drawn through the milk, and the amount of total solid matter on drying at  $100^{\circ}$  is ascertained. The tube is then transferred to a Soxhlet's extractor, and the fat is extracted by a suitable solvent, and weighed in the usual manner. After the extraction is finished, the tube is again dried in the air-bath, thus giving a direct estimation of the non-fatty solids, which can be checked by deducting the weight of the fat from the total solids.

A. H. W.

**Analysis of Chocolate.**—F. Filsinger, Chem. Zeit. 14, 507.

The following results are given for the cacao products, particularly for chocolate :

Melting point of fats . . . . .	29.2°
Hubl's iodine number . . . . .	4.70
Kottstorfer's saponification number . . . . .	248.2
Hehner's fatty acid number . . . . .	91.6
Melting point of fatty acids . . . . .	27.70

**Björklund's ether test :**

3 gms. of the fat dissolved in 6 cc. ether of 0.725 sp. gr. at  $20^{\circ}$  C., leaving a clear solution. After cooling to  $0^{\circ}$ , it was allowed to stand.

At the end of 5 minutes it was	slightly turbid.
“ “ 6 “ “	strongly “
“ “ 8 “ “	milky.
“ “ 9 “	there was a flocculent precipitate.
“ “ 15 “ “	heavy “
settled at the bottom.	

**Filsinger's ether-alcohol test :**

2 gms. of fat with 6 cc. of the ether-alcohol mixture (4 cc. ether, sp. gr. 0.725, and 2cc. alcohol, sp. gr. 0.810) at  $18^{\circ}$  C. did not give a clear solution, but a turbid liquid resembling an emulsion.

S. C.

**The Analysis of Certain Samples of Tinned Meat.**—C. J. H. Warren and C. L. Rose, Chem. News 61, 291 and 303.

The results of an examination of several samples of tinned meats, at the Government Laboratory at Calcutta, are embodied

in this article. The moisture was determined by drying 5 or 6 gms. of pulp in a flat platinum dish, first at  $100^{\circ}$  and then at  $120^{\circ}$ , in an air-bath. After heating several hours, the sample was moistened with absolute alcohol, and again heated, the process of desiccation lasting 8 or 9 hours. 30 or 40 gms. of pulp were similarly heated, and when crisp, were reduced to a fine powder, again heated, and carefully preserved in a bottle for subsequent use. Most of the samples were free from tin and lead. In determining the ash, the pulp used for the determination of the moisture was carbonised below redness, reduced to powder, digested with hot water, and poured on a filter. After thorough washing with hot water, the residue was brushed into the platinum dish, again heated to drive off carbon, then digested with hot water, and the solution was filtered through the same filter. The filter paper was then dried and ignited in the dish. The mixed filtrates, on evaporation and ignition just short of redness, gave the soluble mineral constituents. It was found that the total mineral matter obtained by adding the soluble and insoluble ash, was, as a rule, a trifle higher than the total ash obtained by one operation. The soluble ash was used for the determination of soda and potash, by dissolving in water, adding barium chloride and ammonia successively, heating, filtering off the precipitate, adding ammonium carbonate and oxalate to the filtrate, warming on the water bath, and filtering. The filtrate and washings were then evaporated to dryness and gently ignited to remove ammonium salts. Water was added to the residue, any insoluble matter was filtered off, and the filtrate, after the addition of a few drops of hydrochloric acid, evaporated to dryness with an excess of platinum chloride, this method of treating the ash being essentially the one described by Dr. A. Stutzer ("The Analyst," p. 57, 1885). The alkali metals were determined by the following indirect method: The residue, obtained as above, was treated with alcohol and ether as usual, but instead of weighing the potassium-platinum chloride, it was ignited at a low temperature, with the filter, the residue, exhausted with warm water, thus dissolving out the potassium chloride which was titrated with standard silver nitrate. The alcoholic solution was evaporated to dryness in a small beaker, and the residue washed into a platinum crucible.

Ammonium chloride was then added in excess, the mixture evaporated to dryness, and the crucible cautiously heated, first, without cover, and then covered. The residue was then treated with hot water and the chlorine determined with standard silver nitrate. The two chlorine titrations gave data from which the amount of  $K_2O$  and  $Na_2O$  in the ash could be calculated. Test experiments confirmed the accuracy of this method. For the estimation of chlorine and phosphoric acid, about 20 gms. of the fresh pulp were weighed in a platinum dish, mixed with about 2 gms. sodium carbonate, and dissolved in sufficient water to cover the pulp. The magma was then evaporated to dryness, carbonised below redness, and the residue was extracted, first, with water, and then with nitric acid, the solution being passed through a filter. The residue on the filter was dried, removed to the dish, and ignited until all the carbon was consumed. The ash was treated with dilute nitric acid, the solution being passed through the same filter, and the filtrate and washings collected in a 250 cc. flask. The alkaline solution, after being made faintly acid by acetic acid (the amount of nitric acid used not being sufficient to neutralize the sodium carbonate) was made up to the mark with water. Part of this solution was used for the determination of chlorine, the greater part however, concentrated, and the phosphoric acid precipitated in this as molybdate. Nitrogen was determined in the dried pulp by Kjeldahl's method, and the results calculated back into the moist meat. The albuminoids were calculated from the nitrogen by using the factor 6.25. The boiling water extractive was found by boiling 1 gm. of the dry pulp with distilled water in a 100 cc. flask, and diluting, when cold, to the mark. The liquid was filtered through a dry filter, and a portion of the faintly opalescent filtrate evaporated to dryness in a platinum capsule for dissolved solids. The greater part of the filtrate was measured into an Erlenmeyer flask, placed in boiling water, to evaporate the contained water, and the extractive left as a varnish at the bottom of the flask. Sulphuric acid was then added to the residue in the flask for the estimation of nitrogen. Fat was determined by weighing from .5 to 0.6 grms. into a small accurately stoppered weighing bottle, and adding a measured volume of light petroleum ether from a burette. After di-

gestion, with agitation, for about two days, the mixture was allowed to settle, and a portion of the clear supernatant liquid withdrawn by a small burette, and a measured volume run into a tared beaker. After evaporating off the ether, the residue was dried at  $100^{\circ}$  and weighed, the method being one suggested by Dragendorff, for the estimation of oil (vide, his "Plant Analysis"). The inference from the tabulated results is that tinned meats possess a lower nutritive value than fresh meat. A. H. W.

**On the Estimation of Water in Phenol.**—J. A. Wilson, Chem. News 61, 236.

A sample of crude carbolic acid (i. e., the liquid remaining after the phenol has crystallized, and consisting of cresol and higher homologues) was tested by three methods. 1. By distillation. 2. By agitating 1 volume with 3 volumes saturated salt solution. 3. By agitation with equal parts of 48.50 per cent. sulphuric acid. The per cent. of water found was : 1. 8.6 per cent ; 2. 8.00 per cent.; and 3. 8.25 per cent. The distillation process is considered by the author the best, if the distillate be not observed too late. A. H. W.

**Bottinger's New Reaction for Tannic and Gallic Acids.**—W. Smith, J. Soc. Chem. Ind. 9, 450.

A small quantity of either of the above acids is heated with double its weight of phenylhydrazine for a few minutes at a temperature of  $100^{\circ}$  C., adding a little water, and boiling for a few seconds, and then a drop or two allowed to fall into a beaker containing water made alkaline with caustic soda. The tannic acid gives a beautiful blue color, gradually changing to yellow, while with the gallic acid hydrazine, an orange coloration, was produced. F. R. B.

**Colorimetric Method for Estimating Tannin in Barks, etc.**—Samuel J. Hinsdale, Chem. News 62, 19.

0.04 gm. potassium ferricyanide is dissolved in 500 cc. water and 1.5 cc. of iron chloride (Liquor Ferric Chloride) are added, and this is labeled the "Iron Mixture." 0.04 gms. pure tannin, previously dried at  $100^{\circ}$ , is dissolved in 500 cc. of water, and forms the tannin solution. 0.8 gm. oak bark is exhausted with hot water and made up to 500 cc. with cold water. Six two-ounce

glass tumblers are now placed on a white surface, and in one is dropped from a pipette five drops of the infusion of bark, and in the others, with the same pipette, after rinsing, 4, 5, 6, 7 and 8 drops of the "tannin solution." 5 cc. of the "iron mixture" are now added to each, and in about one minute, 20 cc. of water are added, and at the end of three minutes the shades of color are observed. The number of drops of tannin solution, used in the tumbler which corresponds in shade to the tumbler containing the infusion of bark, indicates the percentage of tannin in the bark. The above process will answer for substances containing less than ten per cent of tannin. The results are in terms for commercial gallotannic acid, and not in those of pure tannin or of the particular tannin in the material assayed. For substances containing between ten and twenty per cent., the infusion is best diluted with an equal volume of water, and the result is doubled. For substances containing less than 1 or  $1\frac{1}{2}$  per cent., exhaust 8 gms., and take one-tenth of the result. The color produced should be a light blue, which is the object of the dilutions. A. H. W.

**Volumetric Determination of Tannin.**—E. Gueney, Chem. News 61, 195 (Comptes Rendus 110, 532).

A solution is prepared consisting of potassium antimony tartrate 12 gms., Porrier's Green 4JE 1 gm., distilled water 1 liter. The antimony salt and the coloring matter are dissolved separately, and the solutions are mixed and filtered. Only the aniline greens are suitable colors, and the one given above was satisfactory. This solution is standardized with a solution of tannin in ether, perfectly pure, and dried previously in a vacuum over sulphuric acid, 5 or 6 gms. per liter being taken for the solution and a little thymol being added to prevent mouldiness. The tannin solution is put in a burette, and 10 cc. of the colored solution of antimony salt and an equal volume of distilled water are put in a glass tube 35 cm. in diameter. The colored solution is raised to a boil and the tannin added until the liquid is completely decolorized, boiling being necessary after each addition of tannin. The green flocculent precipitate, which forms readily, collects and permits of an easy determination of the point of decolorization, when the number of cc. of tannin consumed is read off, and the antimony

equivalent is thus found. This method is readily applicable, it is said, to the analysis of industrial extracts, but as the tannin of these extracts are not identical with the tannin of nut-galls, which were taken as the standard, the richness of an extract will be represented by an equivalent weight of nut-gall tannin, which is the case with all volumetric processes when it is impossible to titrate the liquid with the same kind of tannin which is to be determined. The process is not vitiated by the presence of gallic acid, but is not applicable to the determination of tannin in wines.

A. H. W.

**The Estimation of Glycerine in Soap Lyes and Crude Glycerine.**—O. Hehner, *J. Soc. Chem. Ind.* 8, 4.

Of the various methods now in use, the author considers the bichromate and acetin the most accurate. The acetin method depends upon the conversion of glycerine into triacetin, and the saponification of the latter, which reduces the estimation to an acidimetric operation. 1.5 gms. of crude glycerine is heated to boiling with 7 gms. acetic anhydride and 3-4 gms. anhydrous sodium acetate, in a flask provided with reflux condenser, for  $1\frac{1}{2}$  hours. After cooling, 50 cc. of water are added, and the mixture heated until all triacetin has dissolved. It is then filtered into a large flask, and the residue well washed with water. When the filtrate has cooled, phenolphthalein is added, and the solution neutralized with a dilute (2-3 per cent.) alkali solution, the strength of which need not be exactly known. 25 cc. of a 10 per cent. caustic soda solution, which must be accurately standardized upon normal acid, are then pipetted into the solution, which is heated to boiling for 10 minutes to saponify the triacetin, and the excess of alkali is then titrated back with normal acid. 1 cc. of normal acid equals .03067 gms. glycerine. For the bichromate method, the following solutions are required: bichromate solution, containing about 74.86 gms. of bichromate and 150 cc. strong sulphuric acid per liter. The oxidizing value of the solution must be ascertained by titration with solutions containing known amounts of iron wire.

2. Ferrous and ammonium sulphate solution containing about 240 gms. per liter.
3. A bichromate solution one-tenth as strong as the first. The ferrous solution is standardised upon the chromate





**On a Sophistication of Linseed Oil.**—A. Aignan, Chem. News. 62, 7 (Comptes Rendus 110, 1273). The author proposes a method for detecting resin oil; the usual adulterant in linseed oil, based on the rotatory power which resin oil possesses, and which it communicates to liquids in which it is present. Linseed oil possesses no rotatory power, he states as the result of his examinations of pure oils.

1. *Analysis of a Mixture of Linseed Oil and White Resin Oil.*—Such a mixture turns the plane of polarization to the right by a marked angle, proportionate to the amount of resin oil which it contains. If  $[a]_D$  denotes the rotation observed for a layer 20 cm. in thickness, and  $h$  the weight of resin contained in a weight 100 of the mixture then, for the mixture of linseed oil in refined resin oil,  $[a]_D = + \frac{14}{15}h$ ; for linseed oil and selected white oil  $[a]_D = + \frac{17}{15}h$ ; for linseed oil and fine rectified oil  $[a]_D = + \frac{21}{15}h$ , the first mixture being the most common. In practice,  $[a]_D$  may be measured with the polarimeter, or to value  $h$ , in refined resin oil, according to the formula  $h = [a]_D \frac{15}{14}$ . As the oils in question are deeply colored, a tube of 10 cm. is preferably used, and the formula  $h = [a]_D \frac{15}{17}$  used for finding  $h$ .

2. *Analysis of a Paint.*—(a) A certain quantity of paint is agitated in a flask with ether, allowed to settle, and the ethereal solution is put in the tube of the polarimeter. If  $[a]_D$  is the rotation to the right measured for the thickness of 20 cm., the proportion of resin oil may be calculated by the formula  $h = \frac{[a]_D}{43}$ .

(b) A weight,  $p_1$ , of the ethereal solution, is put in a flask and heated to 100° on the water bath to expel the ether.  $p_2$  is the weight of the oil remaining. Then  $\frac{p_1}{p_2} \times 100 = h$ , for 100 of the mixture of linseed and resins oils contained in the ethereal solution, examined with the polarimeter. If  $h = h_1$  the conclusion is that the paint contained oil of resin without linseed oil. In the ordinary case,  $h_1$  is greater than  $h$ , and  $\frac{h}{h_1} \times 100$  will give the percentage of resin oil contained in the linseed oil which was used in mixing the paint.

A. H. W.

**Iodine Number of Cacao Butter.**—F. Filsinger, Chem. Zeit. 14, 716, has examined a number of brands of this butter, and concludes that the iodine number of pure cacao butter lies between 33.4 and 37.5.

S. C.

**Tests for Adulterations in Wax.**—H. Röttger, Chem. Zeit. 14, 606. The author finds Hübl's\* method to be the most satisfactory. 4–5 gms. of the substance is heated with 20 cc. of 95 per cent. alcohol until it is melted. After shaking it is again heated and titrated with  $\frac{n}{2}$  alcoholic solution of potash using phenolphthalein as an indicator. The number of mg. of potassium necessary to saturate the cerotic acid in 1 gm. wax is called the acid number.

20 cc. of the  $\frac{n}{2}$  potash solution are then added and the flask is connected with an inverted condenser and heated on a water bath until saponification takes place. The product is then titrated back with  $\frac{n}{2}$  hydrochloric acid solution. The number of mg. of potassium used corresponds to the myricyl palmitate and is called the ether number. The acid number plus the ether number gives the saponification number. For pure yellow bees wax, the acid number is found to be between 19 and 21; the ether number between 73 and 76; the saponification number between 92 and 97; and the ratio between the acid number and ether number as 1 : 3.6–3.8. The numbers for bleached wax are within the same limits.

The specific gravity test cannot be depended upon in all cases. For pure yellow, and also the white wax, it varies between 0.956 and 0.964, but in most cases it comes between 0.958 and 0.960. If it is higher than 0.964 it shows the presence of stearic acid, resin, japanese wax, water, heavy spar, brick dust, etc., and if it is lower than 0.956, paraffine, ceresine, or tallow may be looked for.

The methods for detecting stearic acid by separating it as calcium stearate are found to be inaccurate where the amount of stearic acid is less than 10 per cent. because the free cerotic acid that exists in wax will give the same reactions as stearic acid. This difficulty was overcome by Fehling,† whose method the author recommends as the best. It depends upon the fact that cerotic acid is soluble in hot, but insoluble in cold alcohol while stearic acid is soluble in both but separates out by the addition of water. 1 gm. wax is dissolved in 10 cc. 80 per cent. alco-

\*Chem. Zeit. 13, 1375.

†Dingl. Ployt. Jour. 147, 227.

hol by heating a few minutes in a test tube. The solution is then cooled to 20° and filtered into another test tube. Water is added to the filtrate and the two liquids are thoroughly mixed. If stearic acid is present it will separate out and float on top of the liquid.

Most of the methods for the detection of paraffine and ceresine are satisfactory only in special cases. Next to Hubl's method the author finds the one by specific gravity to be the most accurate.

S. C.

**Detection of Methylated Sweet Spirit of Nitre.**—John Muter, *The Analyst* 15, 48.

A simple method, which the author has found to be satisfactory, consists in putting a lump of caustic potash about the size of a small bean into a sample of the spirit and stirring until nearly dissolved. If the spirit is genuine, it will lose all its odor of nitrous ether, after standing for half an hour, and will not have become darker than the palest tint of straw color, and will have the odor of plain rectified spirit. A methylated sample will become of a dark color, varying from deep yellow to orange red, and give off the well known odor of methylated spirit. Should further test be necessary, the author recommends the Miller process, or, putting 10 gms. of the distilled sample that has been treated with potash in the dark for 48 hours with an excess of Hübl's solution. The genuine article absorbs no iodine, while that which has been methylated takes from 4 to 7 per cent.

S. C.

**On the Revision of Constants Employed in the Analysis of Fats and Oils.**—R. T. Thomson and H. Ballantyne, *J. Soc. Chem. Ind.* 9, 588.

Archbutt has observed that olive oils of low density are high in free oleic acid; and on this observation Allen has built the theory that 5 per cent. of free acid diminishes the specific gravity of the oil 0.7. This result is based merely on taking the highest density of pure olive oil (917) and assuming that variations in density are entirely due to free oleic acid. This the authors state is not the case, and that no faith can be placed in the formula for altering the specific gravity of an oil according to the proportion of free acid contained in it. To make sure of this, a sample of

olive oil (sp. gr. 915.6) was treated with a solution of caustic potash in a separator; the soap solution run off, the oil washed with water, and filtered through a dry filter. The density of the acid-free oil thus prepared was only 915.2, so that the free oleic acid (9.42 per cent.) appeared to have raised the specific gravity in the proportion of 0.2 for each 5 per cent. In the iodine absorption test Hübl directs that the absorption should be allowed to go on for two hours, to this Archbutt adds two important suggestions: (1) that at least double the amount of iodine absorbed ought to be present; and (2) that the absorption should be allowed to go on for six hours. In the accompanying table will be found the results of the author's work.

*Table of Constants in the Analysis of Oils.*

Nature of Oil or Fat.	Sp. gr. at 15.5° C. (Water at 15.5°=1000.)	Sp. gr. at 99° C. (Water at 15.5°=1000.)	Iodine Absorp- tion.	KOH Neutralized.	Free Acid.
Olive (Gioja) . . . . .	915.6	..	79.0	19.07	9.42
Olive (Gioja) after removal of free acid . . . . .	915.2	..	79.0	19.07	none
Olive . . . . .	914.8	..	83.2	18.93	3.86
Olive . . . . .	914.7	..	80.0	..	23.78
Olive . . . . .	916.8	..	83.1	19.00	5.19
Olive . . . . .	916.0	..	81.6	..	19.83
Olive (for dyeing) . . . . .	915.4	..	78.9	19.00	9.67
Olive . . . . .	914.5	..	86.4	18.90	11.28
Olive (for cooking) . . . . .	915.1	..	83.1	19.20	4.15
Olive (for cooking) . . . . .	916.2	..	81.2	19.21	not done
Lard (from omentum) . . . . .		859.8	52.1	..	..
Lard (from leg) . . . . .		860.5	61.3	..	..
Lard (from ribs) . . . . .		860.6	62.5	..	..
Beef fat (from suet) . . . . .		857.1	34.0	..	..
Beef fat (oleomargarine) . . . . .		858.2	46.2	..	..
Fat from marrow of ox . . . . .		858.5	45.1	19.70	..
Fat from bone of ox . . . . .		859.2	47.0	19.77	..
Cotton seed . . . . .	923.6	868.4	110.1	..	..
Cotton seed . . . . .	922.5	..	106.8	19.35	0.27
Linseed (Baltic) . . . . .	934.5	..	187.7	19.28	..
Linseed (East India) . . . . .	931.5	..	178.8	19.28	..
Linseed (River Plate) . . . . .	932.5	..	175.5	19.07	..
Linseed . . . . .	932.5	..	173.5	19.00	0.76
Linseed . . . . .	931.2	..	168.0	19.00	..
Rape . . . . .	916.8	..	105.6	17.53	2.43
Rape . . . . .	913.1	..	110.7	17.33	..

Nature of Oil or Fat.	Sp. gr. at 15.5° C. (Water at 15.5°=1000.)	Sp. gr. at 99° C. (Water at 15.5°=1000.)	Iodine Absorp- tion.	KOH Neutralized.	Free Acid.
Rape . . . . .	914.5	..	104.1	17.06	2.53
Rape . . . . .	915.0	..	104.5	17.19	3.10
Rape . . . . .	914.1	..	100.5	17.39	..
Castor (commercial) . . . . .	967.9	..	83.6	18.02	2.16
Castor (commercial) . . . . .	965.3	..	..	17.86	..
Castor (medicinal) . . . . .	963.7	..	..	17.71	..
Arachis (commercial) . . . . .	920.9	..	98.7	15.21	6.20
Arachis (French refined) . . . . .	917.1	..	98.4	18.93	0.62
Lard oil (prime) . . . . .	917.0	..	76.2	..	..
Southern sperm . . . . .	880.8	..	81.3	13.25	..
Arctic sperm (bottle nose) . . . . .	879.9	..	82.1	13.04	..
Whale (crude Norwegian) . . . . .	920.8	..	109.2	..	..
Whale (pale) . . . . .	919.3	..	110.1	..	..
Seal (Norwegian) . . . . .	925.8	..	152.1	..	..
Seal (cold drawn, pale) . . . . .	926.1	..	145.8	19.28	..
Seal (steamed, pale) . . . . .	924.4	..	142.2	18.93	..
Seal (tinged) . . . . .	825.7	..	152.4	..	..
Seal (boiled) . . . . .	823.7	..	142.8	..	..
Menhaden . . . . .	931.1	..	160.0	18.93	..
Newfoundland cod . . . . .	924.9	..	160.0	..	..
Scotch cod . . . . .	925.0	..	158.7	..	..
Cod liver (medicinal) . . . . .	926.5	..	166.6	18.51	0.36
Mineral . . . . .	873.6	..	12.8	..	..
Mineral . . . . .	886.0	..	26.1	..	..
Resin . . . . .	986.0	..	67.9	..	..

F. R. B.

**The Simultaneous Estimation of Saccharose and Raffinose in Commercial Products.**—L. Lindet, Bull. Soc. Chim., 3d Series, 2, 327.

This method is based upon that in which the polarization of the saccharine liquids before and after inversion is used as a means of determining the amount of saccharose and raffinose present. Instead of inverting in presence of acid only, a certain amount of powdered zinc is added, by which constant results are secured.

The solution, containing from 10 to 20 per cent. of the mixed sugars, is placed in a small flask, and the whole immersed in a boiling water flask. About 20 per cent. of powdered zinc is now added, and when the temperature has again reached the boiling

point, 20 per cent. of dilute hydrochloric acid is added. The inversion being completed, the determination is made in the usual way, with the saccharimeter.

The following results were obtained with artificial mixtures :

		Taken.	Found.
1	{ Raffinose . . . . .	.65	.66
	{ Saccharose . . . . .	16.74	16.61
2	{ Raffinose . . . . .	1.21	1.23
	{ Saccharose . . . . .	15.35	15.24
3	{ Raffinose . . . . .	1.67	1.51
	{ Saccharose . . . . .	14.15	14.28

I. A. P.

**The Estimation of Cotton-Seed Oil in Lard.**—Bockairy, Bull. soc. chim., 3d Series, 2, 310.

The author uses the density of lard at 50° as a means of determining the amount of cotton-seed oil present. The different unadulterated lards of commerce possess densities at 50° which vary but slightly from each other. Cotton-seed oil increases the density, differing in this respect from all the other substances used to adulterate lard.

The following tables give the result of the author's experiments :

Name of Product.	Density at 50°.
Lard {	Maximum . . . . . .8915
	Mean . . . . . .890
	Minimum . . . . . .889
Very rancid lard . . . . .	.8895
Oleo-stearine . . . . .	.8885
Renal fat of the ox . . . . .	.8895
New cotton-seed oil . . . . .	.897
Old Cotton-seed oil . . . . .	.896

(2) Mixtures of lard and cotton-seed oil gave results as follows :

New Cotton-seed Oil.	Lard.	Density at 50°.
0	100	.890
10	90	.8915
20	80	.892
30	70	.8925
50	50	.894
75	25	.8953
100	0	.897

Adulterated lards can be examined in this way with facility, and cotton-seed oil detected which would be overlooked by using the ordinary reactions.

The author gives some of his experiments with Hübl's iodine absorption method, but has been unable to get constant results with it.

I. A. P.

**The Detection and Estimation of Albumen.**—G. Potein, Bull. soc. chim., 3d Series, 2, 302.

After naming a number of different methods, and pointing out their defects, the author proposes the following modification of the method most generally used :

The urine is acidulated with acetic acid, and allowed to stand a few hours, to permit the slight precipitate formed to settle on the bottom. It is then filtered and heated to boiling. The boiling liquid is then thrown on a weighed Berzelius filter and washed with boiling acidulated water. The precipitate is dried, and the increase in weight of the filter represents the amount of albumen.

This method can be used with entire success in the case of serine, hydropisine, and egg albumen ; but quite often, as in the examination of urine, other albuminous substances are found along with those mentioned, and which are coagulated by heat and nitric acid, having the general properties of serine, but with this difference, that they are dissolved by the addition of a few drops of acetic acid. For the examination of liquids containing these, the following process is used :

The hydropisine is estimated by precipitating with magnesium sulphate, using only a part of the liquid. In a second part the serine and hydropisine are determined together by heating with a few drops of acetic acid. The filtrate from this will contain the other albuminous matters sought, which can be coagulated with nitric acid.

I. A. P.

## PHYSIOLOGICAL CHEMISTRY.

EDITED BY V. E. VAUGHAN.

**A Ptomaine Extracted from Urine in a Case of "Mumps."**  
—A. B. Griffiths, Chem. News 61, 87.

In the case referred to, the kidneys were involved, and an alka-



loid was extracted by what is called the "ether-tartaric acid" or Luff method. The process is, in detail, as follows:

(a) A considerable amount of the urine is made alkaline with sodium carbonate and then agitated with half its volume of ether.

(b) After standing, the ethereal solution is filtered and agitated with a solution of tartaric acid, which unites with any alkaloids present, forming soluble tartrates, which form the lower layer of the liquid mass.

(c) The tartaric acid solution, after separation from the ether, is made alkaline by sodium carbonate and agitated with half its volume of ether.

(d) The ethereal solution, after standing, is separated, and the ether allowed to evaporate spontaneously.

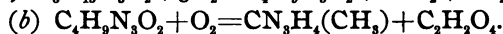
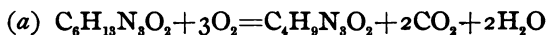
(e) The residue is dried over sulphuric acid and examined for alkaloids (ptomaines).

The alkaloid extracted after this manner, in a case where the parotid and submaxillary glands were both affected, crystallized in white prismatic needles, soluble in water, ether, and chloroform. It had a neutral reaction and a slightly bitter taste, and formed a yellow crystalline platinochloride, a pale yellow aurochloride, and a white crystalline hydrochloride. With phosphomolybdic acid, it formed a golden yellow precipitate, with phosphotungstic acid, a white, with mercuric-potassio-iodide a slight yellow, with iodine a brown, and with picric acid a flocculent precipitate.

An analysis gave results corresponding to the formula



Boiled with mercuric oxide, this base yields creatine (methylglycocyanine) and finally methylguanidine and oxalic acid, according to the reactions following:



Possibly it may be propyl glycocyanine.



The new animal alkaloid is poisonous, producing in a cat to which it was administered nervous excitement, cessation of the salivary flow, convulsions, and death. The alkaloid is not found in normal urines, and the process of its formation is a matter of conjecture.

A. H. W.

**Note on Lead Poisoning by Carbonated Beverages.**—D. Woodman, Jour. Am. Chem. Soc. 11, 99.

The author relates several cases of lead poisoning caused by the use of carbonated beverages. Attention was directed to the stopper of the bottle, which consisted of a rubber washer, held in place by a metal disc. An analysis of the stopper gave 46.0 per cent. lead and 52.2 per cent. tin, which corresponds closely with the composition of common solder. The accompanying table gives the analysis of several samples of soda water, the last sample being a mixture of several different brands. The bottles were kept a week lying on their sides before opening them.

Brand	Quantity Used.	Mgms. of Lead Found.	GRAINS PER GALLON.	
			Lead.	Tin.
I. C. V. . . . .	250 cc.	3.	0.63	—
" . . . . .	250 cc.	2.	0.46	1.4
O. B. . . . .	675 cc.	3.7	0.33	—
V. S. M. H. . . . .	1800 cc.	47.0	1.52	1.63

F. R. B.

**The Peptic and Diastatic Ferments of Micro-Organisms.**  
—Dr. Claudio Fermi, Archiv für Hygiene, B. 10, 1890.

#### PEPTIC FERMENTS.

(a) *The Production of Peptic Ferments by Micro-Organisms.*—The following germs produce ferments which dissolve gelatin and fibrin:

- |                             |                           |
|-----------------------------|---------------------------|
| 1. Anthrax bacillus.        | 7. B. pyocyaneus.         |
| 2. Koch's vibrio.           | 8. Cheese spirillum.      |
| 3. Finkler-Prior vibrio.    | 9. Miller's bacillus.     |
| 4. Micrococcus prodigiosus. | 10. B. megaterium.        |
| 5. Micrococcus ascoformis.  | 11. Hay bacillus.         |
| 6. Bacillus ramosus.        | 12. Tricophyton tonsurum. |

Cultures of the above germs on nutritive gelatine, bouillon, and

potatoes were used for inoculating solidified gelatin. The presence of the ferment is indicated by the liquefaction of the gelatin. The direct action of the germs is prevented by the addition of one or the other of the following disinfecting solutions: Corrosive sublimate, 1-2 per mille; carbolic acid, 3 per mille.; salicylic acid, saturated solution; hydrochloric acid, 5 per mille, thymol, 1 per mille. In one series of experiments the germs were destroyed by fractional sterilization by means of heat. Gelatin plates prepared with these sterilized cultures showed after from 24 to 48 hours from 50 to 100 points of liquefaction which were demonstrated to be free from germs. The gelatin used was as a rule rendered sterile by the addition of thymol. Finally it was demonstrated that the germs fresh from their ferment do not liquefy gelatin.

(b) *Isolation of the Peptic Ferments.*—The peptic ferments of the following germs were isolated:

- |                    |                       |
|--------------------|-----------------------|
| 1. Koch's vibrio.  | 6. B. ramosus.        |
| 2. Finkler-Prior.  | 7. M. ascoformis.     |
| 3. M. prodigiosus. | 8. B. megaterium.     |
| 4. B. pyroyanus.   | 9. Miller's bacillus. |
| 5. Hay bacillus.   |                       |

Some of these ferments were obtained from gelatin, others from potato cultures.

Bacteria which do not liquefy gelatin produce no peptic ferment.

(c) *Properties of the Peptic Ferments.*—These ferments were compared with pepsin, trypsin and papain, with the following results:

(1) The temperature necessary to destroy the bacterial ferments was found to vary as follows:

- |                             |        |
|-----------------------------|--------|
| 1. M. prodigiosus . . . . . | 55° C. |
| 2. B. pyocyanus . . . . .   | 60° C. |
| 3. B. anthracis . . . . .   | 65° C. |
| 4. Koch's vibrio . . . . .  | 65° C. |
| 5. Finkler-Prior . . . . .  | 70° C. |

(2) A temperature of 65° destroys the action of pepsin.

(3) Trypsin heated to 50° no longer digests fibrin, and heated to 60° is without action on gelatin.

(4) At  $+4^{\circ}$  the ferment of Finkler-Prior and trypsin are alike without effect on fibrin.

(5) In the presence of 5 per mille of hydrochloric acid the ferments of Koch's vibrio, Finkler-Prior, *M. prodigiosus*, and *B. pyocyaneus* are without action on fibrin, but still active with gelatin; while under the same conditions trypsin acts upon neither gelatin nor fibrin.

(6) The ferment of anthrax is without action on gelatin in the presence of 5 per mille of HCl.

(7) Papain and the ferment of the Finkler-Prior bacillus alike bear a *dry* heat of  $120^{\circ}$ – $140^{\circ}$  C. without being destroyed.

(8) The presence of corrosive sublimate 1 per mille, of salicylic acid, saturated solution, and of carbolic acid 5 per mille, destroys the activity of the ferments of the cholera germ, the Finkler-Prior bacillus, *M. prodigiosus*, also of pepsin (salicylic acid excepted) and trypsin on fibrin.

(9) The addition of 30 p. c. soda solution does not destroy the action of the cholera ferment, Finkler-Prior, *M. prodigiosus* or trypsin on fibrin.

(10) Pepsin after being treated with a 10 p. c. soda solution for 48 hours is so altered that on the subsequent addition of HCl it is without effect on fibrin.

(11) On the other hand, trypsin, after having been kept for 24 hours in a 30 p. c. soda solution, still digests fibrin, and it digests gelatin after having been kept for 5 days in a 50 p. c., soda solution.

(12) On the addition of 1 p. c., acetic acid, trypsin is without effect on fibrin, but still active with gelatin.

(13) Fibrin kept for 48 hours in a 1 p. c. solution of corrosive sublimate or a 5 p. c. solution of carbolic acid is digested with difficulty by pepsin, and not at all by any of the other ferments.

(14) Trypsin kept for 5 days in distilled water loses its action on fibrin, but not on gelatin.

(15) If trypsin is kept for 24 hours in distilled water at  $37^{\circ}$  with or without the addition of soda, it loses its action on fibrin, but not on gelatin.

(16) Pepsin destroys neither trypsin nor papain.

(17) Of 14 bacterial ferments, only 5 digest fibrin.

(18) Egg-albumen, serum-albumen and diphtheritic membrane are attacked with difficulty by the bacterial ferments.

(19) The bacterial ferments which act on fibrin produce a substance which is not coagulated by heat, but is by  $\text{HNO}_3$ .

(20) Pepton is not necessary for the nutrition of the cells of animals (there is no pepton in the blood) or of micro-organisms.

(21) Gelatin is acted upon much more readily than fibrin by both trypsin and the bacterial ferments.

(22) None of the bacterial ferments act upon fibrin in the presence of hydrochloric acid.

#### DIASTATIC FERMENTS.

(a) *The Production of Diastatic Ferments.*—The following germs were shown to produce very active diastatic ferments :

Anthrax.	B. Fitz.
Cholera.	Hay bacillus.
Finkler-Prior.	B. Megaterium.
Cheese spirillum.	B. tetragenus.
B. ramosus.	Miller's bacillus.

The following produce feeble diastatic ferments :

Faeces bacillus.	Hay vibrio.
B. pyogenes fort.	Steph. cercus et flavus.
B. aceticus.	Pneumonia bacillus.
B. violanus.	Tricophyton tonsurum.
Glanders bacillus.	

With the following, the production of a diastatic ferment is doubtful :

Rabbit septicaemia.	B. diphtheriticus.
B. Zopfi.	B. phosphoresceus.
B. typhosus.	

The following produce no diastatic ferments :

Staph. pyogenes cit.	M. ascoformis.
Rose yeast.	M. prodigiosus.
Soor germ.	B. pyocyaneus.

These were cultivated on mashed potato, and the cultures tested for sugar. The direct action of the germ was prevented, as in the study of the peptic ferments :

(b) *Isolation of the Diastatic Ferments.*—The diastatic ferments of the following germs were isolated :

- |                      |                       |
|----------------------|-----------------------|
| 1. Anthrax.          | 5. B. megaterium.     |
| 2. Cholera.          | 6. Hay bacillus.      |
| 3. Finkler-Prior.    | 7. Miller's bacillus. |
| 4. Cheese spirillum. |                       |

(c) *Properties of the Diastatic Ferments.*—

(1) A temperature of 37° C. favors the culture of the diastatic ferments. However, they are active at +4°, and at 50°.

(2) Heating to 60° destroys the cholera ferment, and to 70° all the others.

(3) Carbolic acid 3 p. c., salicylic acid (saturated solution), and soda solution 10 p. c., do not destroy the diastatic ferments. They are, however, enfeebled by HCl, 5 per mille.

(4) Pancreatic diastase is very much reduced in its activity by acetic acid 1 p. c. and HCl 5 per mille.

(5) Pancreatic diastase retains its activity after having been kept in distilled water for 5 days.

(6) Gum Arabic, inulin, amygdalin and salicin are not affected by the bacterial ferments.

(7) The starches are fermented by the following germs :

- |                   |                      |
|-------------------|----------------------|
| 1. B. Fitz.       | 6. Cheese spirillum. |
| 2. B. megaterium. | 7. B. violaceus.     |
| 3. B. Miller.     | 8. B. pyog. foet.    |
| 4. Cholera germ.  | 9. B. tetragenus.    |
| 5. Finkler-Prior. |                      |

(8) Hay bacillus and B. ramosus change starch into sugar without causing further fermentation.

(9) *M. prodigiosus*, Rose yeast and some other germs which grow well on potato cause no appreciable alteration in the starch.

(10) One and the same germ may produce both peptic and diastatic ferments.

V. C. V.

**Poisonous Products of Sapogenous Intestinal Bacteria.**—Baginsky and Startthagen, *Berliner klinische Wochenschrift*, No. 13, 1890.

The white liquefying bacillus, which is frequently found in the diarrhoeal stools of infants, was grown at 35° C. for ten days on sterilized broth made from horse flesh. At the expiration of this time there was obtained a poisonous base, which agrees very closely with one obtained by Brieger from meat which had been undergoing ordinary putrefaction for four months. This base has the formula  $C_7H_{11}NO_2$ . It forms a double crystalline salt with gold. In addition to the above, there was obtained from the same cultures a poisonous peptone, which caused death in from 48 to 72 hours. Heating this peptone to 100° C. enfeebled, but did not wholly destroy its poisonous properties.

The same germ when grown in sterilized milk does not produce the basic substance mentioned above, but after being kept for three days at 35° C. the unfiltered milk is intensely poisonous. Again, if the milk cultures be kept until complete coagulation takes place, the poisonous properties will be found to have disappeared. The peptone prepared from the milk seems to be quite different from that obtained from the meat culture.

V. C. V.

**The Chemical Poison of Diphtheria.**—Brieger and Frühkel, *Berliner klinische Wochenschrift*, Nos. 11 and 12, 1890.

Bacteriologists now generally agree that the bacillus discovered by Löffler in 1884 is the true cause of diphtheria. Animals inoculated with this germ manifest some of the most characteristic symptoms of the disease, and show after death marked pathological changes. The germ after inoculation subcutaneously is not found save in the immediate vicinity of the place of inoculation. Therefore it has been believed that the systemic effects must be due to the production of a soluble poison. The first attempt to determine the nature of this poison was made by Löffler in 1887. He grew the germ in two flasks of bouillon containing peptone

and grape sugar. The contents of one flask were evaporated to 10 cc. on the water bath, and this residue was found not to be poisonous. The contents of the second flask were extracted with ether, and this extract was also found to be inert. Next he extracted a meat-broth culture of the germ with glycerine, precipitated the extract with five times its volume of absolute alcohol, and obtained an abundant, flocculent precipitate, which, after being washed with alcohol and dissolved in water, produced in guinea-pigs necrosis at the point of inoculation. From these results, Löffler concluded that the poison of diphtheria is an enzyme.

The next attempt to ascertain the true nature of the poison was made by Roux and Tersin. They passed bouillon cultures of the bacillus through a Chamberland filter, and found that the germ-free filtrate was poisonous. On being heated to 100° C. for twenty minutes, the filtrate became inert, and on being heated to 58° C. for two hours, its virulence was greatly diminished. The poisonous principle was precipitated by alcohol, then placed in a dialyser, and the poisonous principle was precipitated, or carried down mechanically, by treating the dialysate with calcium chloride. From these results, Roux and Tersin conclude that the poison is a diastase, enzyme, or similar substance.

At this point, the work has been taken up by Breiger and Fränkel. They employed germs taken directly from diphtheria membranes. They have demonstrated, confirmatory of the work of Roux & Tersin, "that Löffler's diphtheria bacillus elaborates in cultures a soluble, poisonous substance, separable from the germ itself, which produces in susceptible animals the same symptoms which follow inoculation with the living germ. Further, that this substance is destroyed at a temperature above 60°, while it remains intact when the solution is evaporated at 50°, even in the presence of an excess of hydrochloric acid. The last fact shows that the poison is not a ferment or enzyme." The only basic substances which could be found were trace of kreatinin and cholin, therefore the poison is not a ptomaine. By distillation at from 20°-35° in vacuo, only inert substances were obtained. Further study showed that the poison, after precipitation with alcohol and resolution in water, was precipitated by saturation with ammonium sulphate. Dried at 40° in vacuo, it remained active. It



contains sulphur, and responds to Millon's and the biuret test, therefore it must be an albuminous body. It is not precipitated by saturation with magnesium sulphate, and therefore cannot be a globuline. Further, it is not precipitated by sodium sulphate, sodium chloride, or dilute nitric acid. It is precipitated by the concentrated mineral acids, by potassium ferrocyanide and acetic acid, by phenol, the organic acids (in excess of which it redissolves), copper sulphate, silver nitrate, mercuric chloride, and the general alkaloidal reagents.

An ultimate analysis calculated from the ash-free substance gave the following results: C 45.35, H 7.13, N 16.33, S 1.39, O 29.80.

Contrary to the French observer, Brieger and Fränkel found that the substance obtained by them did not diffuse through parchment.

The toxic albumen of diphtheria bears some resemblance to the ichthyotoxicum obtained by A. and U. Mosso from the serum of certain mureniden. Kobert and Stillmark have also found poisonous albumens in the vegetable kingdom. These are called by Martin phytalbumoses. Hankin has obtained an albumose from cultures of the anthrax bacillus, which rendered animals innocuous to the disease. Christmas from cultures of the staphylococcus pyogenus aureus precipitated with alcohol an albuminous substance which, when injected into the anterior chamber of the eye or under the skin, produced suppuration. However, these substances are probably globulins, and are soluble, though very slowly, in dilute solutions of common salt. It is well known that some years ago Mitchell and Reichert found in the venom of serpents two poisonous proteids, a globulin and a peptone.

The subject of poisonous proteids promises to be one of great importance and interest.

V. C. V.

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THE

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# Journal of Analytical Chemistry.

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## COMMERCIAL VALUATION OF CREAM OF TARTAR SUBSTITUTES.

BY CHARLES A. CATLIN, PROVIDENCE. R. I.

Few questions are more perplexing to the analyst than the commercial valuation of cream of tartar substitutes, and more especially of those containing acid phosphate preparations.

The ordinary methods of titration with standard alkali, either directly or indirectly employed, fail to give the proper data, even with the phenolphthalein indicator, as may be readily shown on taking the sample and bicarbonate of soda in the proportions thus indicated and boiling up together in water, when it will be found that the reaction is incomplete, a greater or less proportion of the carbonic acid failing of evolution, the amount varying in the same sample with the quantity of water employed, the temperature to which the mixture is submitted, and the length of time through which it endures.

Other things aside, the value of a baking acid is of course in its power of evolving carbonic gas from alkaline bicarbonate when in admixture therewith under the conditions in which it performs its office in the bread-making process; and since, as we have seen varying conditions have decided influence upon such reaction, it is apparant that no method of valuation can have real utility that does not take into account, and as far as possible, initiate the actual baking process in these essentials.

To inform myself more exactly, I made many careful observations of the steps pursued by a cook of the best home spun order, in preparation of baking-powder biscuit dough and subsequent baking of the same. I found that she was using about 504 gms. of flour (Haxall brand) for the quart, as leavening for which

two heaping teaspoonfuls of a popular brand of baking powder, weighing together about 17 gms., and for moistening, 386 gms. of either milk or water, or about 23 cc. of liquid for each gram of baking powder employed.

The range of temperature and the length of exposure thereto were noted as follows: When the dough was ready for baking, a thermometer was inserted so that the bulb might be held as near as possible at the centre of the biscuit or loaf, and the whole placed in the already heated oven by the cook in the usual manner, the range of the temperature being observed through a peephole, and record made thereof at stated times.

Averaging a series of accordant results thus obtained, I found the oven at the outset to have a temperature of about 380° F., and that the temperature of the interior of the dough passed through the following range:

After 1 minute's exposure in the oven . . . . .	95° F.
" 3 " " " " . . . . .	130° "
" 4 " " " " . . . . .	150° "
" 5 " " " " . . . . .	160° "
" 7 " " " " . . . . .	205° "
" 10 " " " " . . . . .	205° "
" 12 " " " " . . . . .	210° "
" 13 " " " " . . . . .	212° "
" 15 " " " " . . . . .	212° "
" 17 " " " " . . . . .	217° "

After thirteen minutes' exposure, the cook pronounced the biscuit "done," but for the sake of the experiment, the heating was continued, when after fifteen minutes the crust had become far too brown to be palatable, while at the end of seventeen, actual burning had well commenced. From the above it is apparent, then, that in the actual baking process the temperature of the dough is raised gradually, through a lapse of about thirteen minutes, to a temperature of not more than 212° F., and for a successful issue, this should not endure for more than one minute, if indeed it should be allowed to continue for that length of time.

Consideration of these conditions of the actual baking process has led me to adopt the following method for determining the value of cream of tartar substitutes generally and more especially of those having so-called acid phosphate as the active agent:

The first step is to determine the neutralizing power of the sample by titration with caustic alkali, using phenolphthalein as the indicator. To do this, weigh one gm. into a 300 cc. titrating flask, run in upon it 100 cc. of water, add 1 cc. of phenolphthalein solution (1 gm. in 250 cc. equal parts alcohol and water), agitate a few minutes to effect complete solution or dissemination of the sample, and then titrate with normal caustic alkali to light pink coloration. The amount of solution used to effect this is noted, a further addition is made in excess, and the whole brought to a rapid boil and kept there for a few minutes. If now the pink color has faded out, a further addition of alkali is made, and another moment's boiling allowed, and so on till a permanent pink color is obtained, noting of course the alkali used. It is my custom to make these additions a cubic centimeter at a time, and in most cases I find the first excess of 1 cc. sufficient. While the solution is still hot, add in cc. quantities normal sulphuric acid, and then titrate back to light pink with the normal alkali. If normal solutions are used, the statement will then be: Total alkali, less acid added, equal neutralizing power of one gram of sample. From this calculate equivalent bicarbonate of soda.

As there is found to be no definite ratio between the neutralizing capacity of these preparations and their gas evolving power when in admixture with alkaline bicarbonate under the conditions of the baking process, and since this alone is the measure of their efficiency, their valuation should depend upon the determination of this quality. To arrive at this, weigh into a perfectly dry flask one gm. of the sample and also the exact equivalent of pure bicarbonate of soda as indicated by the titrating process. Perfectly bicarbonated soda is scarcely to be found, but it may be obtained very nearly by precipitation from a strong solution of pure monocarbonate supersaturated with carbonic acid, drying the salt with bibulous paper as far as possible, then powdering, and finally drying over oil of vitriol, under a bell glass, in the ordinary manner. Thus prepared, it is hardly necessary to make allowance for the slight trace of monocarbonate which seems to be all but unavoidable. Its carbonic acid strength should be carefully determined, however, for accurate work. The flask, fitted with the usual stoppered funnel and exit tube, into which has been weighed

the charge of sample and its equivalent bicarbonate, is attached to a carbonic acid absorption apparatus of any of the well known types.

Personally I much prefer the soda-lime tubes to the potash bulb, but this is a matter of individual experience.

In the actual baking process, we found that 23 gms. of water were employed for each gm. of baking powder used. A large part of this water must have been practically inert in bringing about reaction between the constituents of the powder, being absorbed by the flour. Just what that loss of water would be, we have not the means of determining, but certainly not more than half the water employed can be considered as exerting solvent action upon the powder. I would therefore recommend that not more than 20 cc. be used for each gm. of acid sample and its soda bicarbonate equivalent. A very much larger amount would so alter the conditions of reaction that unreliable results would be the consequence. A very much smaller amount would be impracticable to use. In the flask, after attaching the absorption apparatus, introduce therefore through the funnel tube, 20 cc. of water, and disseminate the powder through it by careful agitation of the whole. We have seen in our observation of the baking of the biscuit, that in the matter of temperature,  $212^{\circ}$  F. is never exceeded within the dough in proper manipulation, and that limit should never be allowed to endure for more than one minute at the longest. As a matter of fact, I believe that when the temperature reaches  $200^{\circ}$  F., or even a much lower point, the dough has attained such a consistency that further evolution of gas is rather an injury than an advantage. However this may be, it is certain that gas evolved beyond the limit of a temperature of  $212^{\circ}$  F., enduring for one minute, is of no practical value. The contents of the flask is therefore gradually raised to the boiling point, and as we have observed in the baking process, maintained at that temperature not longer than one minute, then aspirate the flask and note the increased weight of the absorption tubes, which gives us then the amount of carbonic acid evolved under the baking conditions, and is consequently the correct measure of strength of the sample for the purpose for which it is designed. Knowing the carbonic acid contents of the bicarbonate of soda used, the results

obtained as above may be readily checked by again attaching the absorption tubes to the flask and running in through the stoppered funnel a few cc. of dilute sulphuric acid, whereby the remaining carbonic acid will be evolved. Aspirating the apparatus again, the total increase in weight of the absorption tubes above the first weighing should correspond with the calculated amount of carbonic acid in the bicarbonate of soda used.

This last step suggests a more rapid method of procedure:

Find the neutralizing power of the sample as before, then into the flask of the carbonic acid apparatus weigh one gram and its equivalent bicarbonate of soda, add the 20 cc. of water, bring the whole to a boil and keep it at that temperature not longer than one minute, the flask being detached from the absorption tubes meanwhile, blow out the flask to remove all of the carbonic acid thus evolved, then attach to the absorption apparatus and determine the carbonic acid still remaining unevolved by adding the dilute sulphuric acid, etc., as before. The carbonic acid thus obtained, deducted from the total calculated carbonic acid of the bicarbonate of soda employed, gives the gas evolving power of the sample under the conditions of the baking process.

For a convenient statement of results, I would suggest taking the carbonic acid equivalent of one gram of pure bitartrate of potassium, i.e. 0.2340 gms., and expressing results in thousandths of that standard, obtained by removing decimal point, adding three 0 to the amount of carbonic acid carried to tenths milligrams and dividing by 2340.

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## THE PROPER STANDARD FOR THE ATOMIC WEIGHTS.

[A Paper read before the American Association for the Advancement of Science.]

BY F. P. VENABLE.

Among the important questions attracting the attention of chemists to day is that of the proper standard to be adopted for the atomic weights. It is a question whose settlement cannot be much longer postponed without injury. It must be settled by careful consideration on the part of associations and individuals, and then by general usage—a sort of majority vote. I therefore venture to bring the question in its present status to the atten-

tion of this body of chemists, asking a careful, thoughtful discussion and consideration of it.

Two elements lay claim to the position of standard for all other atomic weights, hydrogen and oxygen. Hydrogen is called by Meyer and Seubert the Dalton-Gmelin unit and oxygen the Wollaston-Berzelius unit. The contention is an old one then, and first one then the other has been forced to give way in the struggle. For a long time oxygen was the accepted standard of the only approximately accurate atomic weights—those of Berzelius. It was then displaced by hydrogen, and this element has so fixed itself in the literature that it cannot well be in turn displaced as the unit. But I would make a careful distinction between unit and standard. To make a radical change now would be inconvenient and difficult, and should be done only under stress of absolute need. When one considers the difficulty and tediousness of becoming accustomed to new numbers and the decrease in value and intelligibility of all the literature in the old notation that would follow a change of unit, one can properly realize the cost of such a change.

We are closing a century's labor, however, and a century's history, and it is important that we should come to some agreement on this point, and so be in a position to confer some degree of constancy upon our so-called constants. As it stands now each revision, or redetermination, is calculated by two standards, and the individual chemist is left to choose between them at his own sweet will. There is no necessity for this, and it is a blot upon our science. Other sciences, notably electricity, are getting their standards in order, their loins girt, as it were, for the race of the twentieth century. We must settle this question, as well as others, if we would move freely in the grand onward march.

The best settlement comes, as is so often the case, in the way of a kind of compromise. Let oxygen be the standard and hydrogen practically the unit. This reduces the changes to the least possible, and tables arranged on this basis have been in use a long time. In fact, it was only with the idea of securing greater accuracy that this arrangement was ever changed. The use of  $O = 15.96$  as a factor for calculation appeared about the time of the first appearance of Meyer's work on the Modern Theories of Chemistry, and is mainly due to his instrumentality. The

pursuit of accuracy in that direction has proved an *ignis fatuus*, and the necessity for something more fixed becomes every day more and more apparent.

The extent of this need impressed me greatly while studying the various recalculations of the atomic weights as made by our own Prof. Clarke, Meyer and Seubert, Sebelien and Ostwald, and lead to an article on the subject first published by the Elisha Mitchell Scientific Society, and afterwards by the *Chemical News* and the *JOURNAL OF ANALYTICAL CHEMISTRY*.\* This seems to have been the first article published in the discussion, but to Dr. Brauner, of Prague, belongs the credit of arousing the discussion which was carried on in the *Berichte* of the German Chemical Society during 1889, and which was participated in by Ostwald, Meyer and Seubert, and Brauner.† Meyer and Seubert alone opposed the adoption of  $O = 16$  as the standard.

Without dwelling separately on these articles, or the arguments adduced on one side and the other, I shall content myself with trying to state clearly the reasons for adopting  $O = 16$  as the standard. Were it a mere matter of sentiment, of securing a larger number of integers in the table of atomic weights, or something of that kind, I think all will agree with me that the change would be mere folly. Such men as Ostwald and Brauner would not waste time quibbling over anything so insignificant. There must be and is something deeper, and it is strange to me that Meyer and Seubert seem unable to see the true point of contention.

The facts of the case are as follows: Hydrogen, as having the least atomic weight, seems, at first sight, the most appropriate unit for measuring the others. It admits of all being represented by numbers greater than unity, and none of them of such inconvenient size as in the Berzelius table with  $O = 100$ . If we could determine the ratio of the other elements to hydrogen directly, that is, if their atomic weights were determined by means of hydrogen, and hence were directly dependent upon this as unit, there would be nothing further for us to desire. Unfortunately, very few such direct ratios can be secured. Only three or four have been determined.

\*See Vol. 3, p. 48.

†See also *Chem. Zeit.* 1890, No. 13, where Dittmar says: "Ich wage zu hoffen, dass diejenigen Chemiker, welche seither, nachdem sie die Ueberzeugung gewonnen hatten dass  $O : H$  kleiner ist als 16, darauf bestanden haben, dass  $H = 1$  als einheit für die Atomgewichte festgehalten werden müsse, diese absurde Praxis aufgeben und den 16 Theil des Atomgewichtes des Sauerstoffs als einheit adoptiren werden."



Under these circumstances, two things are possible. First find the ratio between hydrogen and oxygen, then, using this as a factor, calculate the other atomic weights. Could we find this ratio absolutely, there would be no objection to this method, but it is impossible to eliminate or allow for personal and experimental errors. The ratio found can at best be but an approximation. Evidently, by using an approximation to calculate other approximations, we get further and further from the truth. As Ostwald has said, we are introducing totally uncalled for and unnecessary errors, and he is right in styling it, in this stage of our science, a barbarism. As Brauner has pointed out these errors can easily amount to several integers in the higher atomic weights.

It is not for lack of skilled workers to undertake the determination of this ratio. Much excellent work has been done upon it, and especially in the last two or three years. Ostwald has summed these up, and says there is an error of at least 0.3 per cent. which has not been removed by recent workers. Brauner agrees with him that the variations are irreconcilable, and though Meyer and Seubert think the ratio can vary but little from that assumed by them as justifiable by the best determination, it is manifestly a point on which the best authorities differ and hence one of uncertainty.

Why should we then make use of the number 15.96 if it is not fixed by incontrovertible, unerring, universally accepted experiments. It makes the matter no whit better for Meyer and Seubert to profess their willingness to recalculate their table should a change in the number 15.96 prove necessary. It is merely a confession of the insecurity of their own position. We do not wish any recalculation. We wish a standard by which the calculations can be made once and for all, one that will give us the least possible error and is itself independent of other calculations. The present use of the double standard 15.96 and 16 seems puerile and leads to all manner of inaccuracies.

The second possibility is to use oxygen as the standard.

The question reduces itself, then, really to this: Shall we use  $O=15.96$  or  $O=16$ ? For oxygen must be used from very necessity. If  $O=15.96$  is not the absolute ratio or is not generally accepted as such then the reason for its use ceases.

It is not necessary to bring forward arguments as to the rela-

tive convenience of the two, nor as to their effect upon the periodic law. Such arguments have little weight or significance when it is seen that the question lies between  $O=15.96$  and  $O=16$ , and that hydrogen can never be the actual standard or factor from purely chemical reasons. Nor yet is there much in any argument from analogy with other standards and units. Such only lead us away from the one all-important consideration—the avoidance of unnecessary errors.

I have said that the present proposition could be looked upon in the light of a compromise. If oxygen takes the place of hydrogen as standard, what falls to the share of the latter element? If oxygen were made 100, as in the Berzelius table, or 10 or 1, as have been proposed, then the present numbers, as referred to hydrogen, would be entirely changed and lost sight of. The plan is to change them as little as possible, giving oxygen the number sixteen, which was once regarded as the ratio between it and hydrogen, and, according to the views of some, may still be it. Then the number for hydrogen will vary very little from unity, and the whole table is nearly based upon it as the unit. This number will change from time to time with new determinations, but such changes will involve no others. Oxygen, the standard, will then be fixed, and our task lies in the accurate determination of the others by it.

Meyer and Seubert cling to the idea that if oxygen be adopted it must be taken equal to unity, maintaining that  $O=16$  is neither flesh nor fowl, and by no means a unit. It is true that the standard or basis of a series of physical constants has in the past usually been taken equal to unity, but I cannot conceive the power of this habit to be sufficiently strong to force us into inconveniences or inaccuracies. That it is not regarded as a binding rule, has been shown by the choice of some recent standards, especially in the new science of electricity.

The atomic weights are but relative numbers. To be in any respect constants, they must be relative to but one single element. With but few exceptions, the ratio to oxygen can be determined. In revision of atomic weights, then, this should receive the chief attention and the oxygen ratio should be most carefully and directly determined.

Where the intermediation of another element is made use of

(even though this be one which "may be counted among those of which the atomic weights are already known with the nearest approach to exactness," as Dr. Mallet recommends,) it must be borne in mind that the result is subject to a certain error, which is generally multiplied several times and hence cannot give concordant results with the direct oxygen ratio and less stress must be placed upon it. If the well determined ratio H:O is subject to an error of 0.3 per cent., how much greater is the error in the case of ratios less well known.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE. FROM H. W. WILEY.]

## XII.—SOME NOTES ON THE DETERMINATION OF SUGARS WITH FEHLING'S SOLUTION.

BY H. E. L. HORTON.

In the course of work on carbohydrates, one of the reagents most used is the so-called Fehling solution, and the question arises as to the Fehling solution to be used, for there exists in literature a great number of solutions.

Tollen's,\* in his Handbuch, says, in speaking on this point: "Sie sind jedoch, weil nicht ganz gleich zusammen gesetzt, auch nicht ganz gleichwerthig, und man muss, wenn man eine der unten näherangegeben Tabellen benutzen und ganz genaue Resultate erhalten will, die von dem betreffenden Autor benutzte Fehlingsche Lösung anwenden."

The use of the copper test in quantitative determinations of sugars is an old method, and proposed by several chemists, viz., Barreswill,† Falsk,‡ Scharlau,§ but until 1848, when Fehling's article appeared in the Archiv für Pysiol. Heilkunde, there existed nothing definite.

Tollens and Rodewald have published a table in which they give the many solutions suggested from time to time, and for purposes of future reference it seems desirable to give this table again, with a few additions.

\*Kurzes Handbuch der Kohlenhydrate, S. 72.

†Osterlen's Jahrbücher für prak. Heilkunde, 1845, No. 4, p. 509.

‡Falsk, Broschüre die Zucker-Hahnrohr, Berlin, 1846.

§Jour. de Pharm. et de Chem. Serie III, Tome 6, 301, 1844.

	Quantity of Alkali.	REMARKS.
1. ALLIHN :		
34.6 gms. copper sulphate and solution, made up to 500 cc.	125 gms. KOH (equivalent to 89.2 NaOH.)	
173 gms. potassium-sodium tartrate.		
125 gms. potassic hydrate and solution made up to 500 cc.		
2. A. H. ALLEN :		
34.64 gms. copper sulphate and solution made up to 500 cc.	70 gms. KOH.	
180 gms. potassium-sodium tartrate.		
70 gms. sodium hydrate (not less than 97% NaOH) and solution made up to 500 cc.		
3. BÖDEKER :		
34.65 gms. copper sulphate.	67.3 gms. NaOH.	0.180 gms. grape sugar reduce according to Bödeker. 36.1 cc. copper solution equals 0.397 gms. copper oxide. The same quantity milk sugar reduces, however, only 27 cc. Copper solution equals 0.298 copper oxide.
173 gms. potassium-sodium tartrate.		
480 cc. sodic hydrate solution, 1.14 sp. gr. Fill to liter.		
4. M. BOUSSINGAULT :		
40 gms. copper sulphate.		
160 gms. tartrate of potash.		
130 gms. sodium hydrate.		
5. DIETZSCH :		
34.65 gms. copper sulphate.		
150 gms. potassium-sodium tartrate.		
250 gms. sodic hydrate solution, 1.2 sp. gr.		
150 gms. glycerine.		
6. FLEISCHER :		
69.278 gms. copper sulphate dissolved in about 500 cc. water, and to this 200 gms. tartaric acid. Fill to liter with concentrated sodic hydrate solution.	Indefinite Amounts.	20 cc. copper solution equals 40 cc. sugar solution that contains in every cc. 5 mgs. grape sugar.

	Quantity of Alkali.	REMARKS.
7. After FEHLING : 40 gms. copper sulphate. 160 gms. di-potassium tartrate. 600-700 gms. sodic hydrate solution, 1.12 sp. gr. Fill to 1154.4 cc. solution.	54.6-63.7 NaOH.	
8. v. GORUP-BESANEZ : 34.65 gms. copper sulphate. 173 gms. potassium-sodium tartrate. 480 gms. sodic hydrate solution, 1.14 sp. gr. Fill to liter.	67.3 NaOH.	
9. GRIMEAUX : 40 gms. copper sulphate. 160 gms. potassium-sodium tartrate. 600-700 gms. sodic hydrate solution, 1.20 sp. gr. Fill to 1154.4 cc.	92.5-107.9 NaOH.	10 cc. of this solution is completely decolorized by 5 centigrams glucose.
10. HOLDEFLEISS : 34.632 gms. copper sulphate in one liter water. 125 gms. potasic hydrate. 173 gms. potassium-sodium tartrate. Fill to liter.	125 gms. KOH (equivalent to 89.2 NaOH).	
11. HOPPE-SEYLER : 34.65 gms. copper sulphate. 173 gms. potassium-sodium tartrate. 600-700 cc. sodic hydrate solution, 1.12 sp. gr. Fill to liter.	63.0-73.5 gms.	From the above given Fehling solution 1 cc., reduces to copper oxide exactly 5 mgms. grape sugar.—Handbuch. p. 284.
12. KROCKER : 6.28 gms. copper sulphate. 34.6 gms. potassium-sodium tartrate. 100 cc. sodic hydrate solution, 1.14 sp. gr. Fill to 200 cc.	70.1 gms.	In this solution is contained 0.346 gm. copper sulphate, which is reduced by 0.050 gm. grape sugar.—Leitfaden, p. 126.

	Quantity of Alkali.	REMARKS.
13. LIEBERMANN : gms. copper sulphate. 20 gms. potassium-sodium tartrate. 70 gms. sodic hydrate solution, 1.12 sp. gr. Fill to 115.5 cc.	107.8 gms.	
14. LÖWE : 15 gms. copper hydrate. 60 gms. glycerine. 80 cc. sodic hydrate, 1.34 sp. gr. 160 cc. water. Fill to 500 cc.		
15. MOHR : 34.64 gms. copper sulphate. 150 gms. dipotassium tartrate. 600-700 cc. sodic hydrate solution, 1.12 sp. gr. Fill to liter.	70.5-82.3 NaOH.	
16. MÄRCKER : 35 gms. copper sulphate and solution made up to liter. 175 gms. potassium-sodium tartrate. 125 gms. potassic hydrate and solution made up to one liter.	125 gms. KOH. (equivalent to 89.2 NaOH.)	
17. MAUMENE : 375 gms. copper sulphate. 188 gms. potassium-sodium tartrate. 166 gms. potassium hydrate. Fill to 9 liters.		
18. MONIER : 40 gms. copper sulphate. 3 gms. ammoniac chloride. 80 gms. cream of tartar. 130 gms. NaOH. Fill to liter.	130 gms.	10 cc. = 0.0577 dextrose. = 0.0548 canesugar.

	Quantity of Alkali.	REMARKS.
19. NEUBAUER & VOGEL : 34.639 gms. copper sulphate. 173 gms. potassium-sodium tartrate. 500-600 gms. sodic hydrate solution, 1.12 sp. gr. Fill to liter.	52.5-63 gms.	
20. PASTEUR : 40 gms. sulphate of copper. 105 gms. tartaric acid. 80 gms. potash. 130 gms. soda.	210 gms.	
21. PASSOZ : 40 gms. copper sulphate. 300 gms. rochelle salt. 29 gms. NaOH. 159 gms. $\text{HNaCO}_3$ . Fill to 1 liter. Allow to stand 6 months before use.	29 gms.	1 cc. = 0.0577 gms. dextrose. 1 cc. = 0.0548 gms. cane sugar.
22. RIETH : 34.64 gms. copper sulphate. 143 gms. potassium-sodium tartrate. 600-700 cc. sodic hydrate solution, 1.12 sp. gr. Fill to liter.	70.5-82.3 gms.	
23. RODEWALD & TOLLENS: 34.639 gms. copper sulphate and solution made up to 500 cc. 173 gms. potassium-sodium tartrate. 60 gms. sodium hydrate ("sticks") and solution made up to 500 cc.	60 gms. NaOH.	
24. SCHORLEMMER : 34.64 gms. copper sulphate. 200 gms. potassium-sodium tartrate. 600-700 cc. sodic hydrate solution, 1.20 sp. gr. Fill to liter.	128.1-149.5 NaOH.	

	Quantity of Alkali.	REMARKS.
25. SOXHLET :		
34.639 gms. copper sulphate and solution made up to 500 cc.		
173 gms. potassium-sodium tartrate.	51.6 gms. NaOH.	
51.6 gms. sodium hydrate and solution made up to 500 cc.		
26. SOLDAINI :		
3.464 gms. copper sulphate plus 5 aq.		
297 gms. potassium acid carbonate. Fill to liter.		
27. VIOLETTE :		
(Variously given.)		
34.64 gms. copper sulphate.		
187 gms. rochelle salts.		
78 gms. sodic hydrate, made up to one liter.	78 gms. NaOH.	10 cc. = 0.0500 dextrose. = 0.0475 cane sugar
See, also, Dosage du sucre Paris, Gauthier - Villars, 1868.		

1. Allihn.
2. Allen : Commercial Organic Analysis.
3. Bödeker : Henle's u. Pfeufer's Zeit. für Rationelle Med. VI, 2, 1855. Jahresbericht über die Fortschritte d. Chemie, 1855, 818.
4. Boussingault.
5. Dietzsch.
6. Fleischer : Titrimethode, 1871, S. 226.
7. Fehling : Ann. Chem. und Pharm. Bd. 72, 106.
8. Gorup-Besanez : Anleitung zur Qual. u. Quant. Ch. Analy. 3 Auf. 1871, 460.
9. Grimeaux : Chemie Organique 1872, 248.
10. Holdeffleiss : Landwirtsch. Jahrbücher Supp. 1877, 130.
11. Hoppe-Seyler.
12. Krocke : Leitfaden f. d. Qual. & Quant. Chem. Anal. 1868, 125.
13. Liebermann : Chemische Untersuchungen auf dem Gebiete der Medicinalpolize, S. 222.
14. Löwe : Zeit. für anal. Ch. 10, 453.
15. Mohr : Lehrbuch der Titrimethode, 3 Auf., 1870, 438.
16. Märcker : Handbuch der Spiritus fabrikation, 1877, S. 81.
17. Maumene.
18. Monier.
19. Neubauer & Vogel : Analyse des Harns, 7 Auf., 206.
20. Pasteur.
21. Passoz.
22. Rieth : Die Volumetrie, S. 305.
23. Rodewald u. Tollens.
24. Schorlemmer : Kohlenstoffverbindungen, 1871, 349.
25. Soxhlet : Jour. prakt. Ch. XXI, 227.
26. Soldaini : L'Orosi, 12, 196-198; Chem. Centr. 1889, ii, 389-390.
27. Violette : Dosage du Sucre Paris, 1868.



The question arises, "What is Fehling's solution?" When we speak of Fehling solution it is with no particular idea in mind as to one solution, and it is here that a reform is necessary. Prof. Soxhlet in his classical work on "Das Verhalten der Zuckerarten zu alkalischen Kupfer u. Quicksilberlösungen," has given us the data obtained when using a particular solution, but too often some one comes out with a new Fehling solution with no data as to its reducing power. At present the best known sugar chemists in Germany are using the solution used by Soxhlet, the English chemists, many of them follow Allen, the French and American chemists use the Viollette solution. This want of uniformity is to be deprecated; we must use the same solution if we expect comparable results. The Germans have a solution worked out with a completeness to be admired, and have the analytical data necessary for such a solution, while on the other hand the chemists using other solutions have as yet no accurate data. It will be of interest to quote Fehling's publication, which appeared in Ann. LXII, 108:

"40 gms. reiner krystallisirter kupfervitriol werden in etwa 160 gms. Wasser gelöst; anderseits wird eine Lösung von 160 gms. neutral weinsäurem Kali in wenig Wasser gelöst mit 600-700 gms. kaustischen Natronlauge von 1.12 sp. Gew. versetzt und zu dieser basischen Lösung nach und nach die Kupfervitriollösung gesetzt; ich verdünne dann das Ganze auf 1154.4 cm. bei 15° C."

To grasp this more readily we can state it thus:

40 gms. copper sulphate.

160 gms. neutral potassium tartrate.

600 to 700 cc. sodic hydrate solution of 1.12 sp. gr.  
(54.6-63.7 gms. solid NaOH),

and fill up to 1154.4 cc. This number 1154.4 cc. was not originally used by Fehling he having used 1000 cc., but for convenience in calculation the number 1154.4 was adopted. Bödeker gave himself the trouble to calculate these quantities to a liter.

From an examination of the table it will be seen how the quantity of alkali changes in the different solutions and it would appear that work carried on using such solutions cannot be relied on.

Tollens and Rodewald in the course of work on milk sugar have observed that the quantity of alkali influenced the results and they write:

“Demnach hängt das resultat von dem Verhältniss zwischen Kupfer und Natriumhydroxyd ab, und daraus folgt, dass das Verhältniss in der Fehling'schen Lösungen durchaus nicht gleichgültig ist.”

It is easy to see the necessity for some work in this direction and this paper is the first of a series on the subject of the use of Fehling solution in determining sugars.

*Copper Sulphate Solution used in Experiments.*—The copper sulphate used was obtained by dissolving copper in sulphuric acid and repeatedly recrystallizing the product. The final product was dried between folds of filter paper and then allowed to stand in air for two days. A water determination showed the proper amount of crystal water.

34.639 gms. of this salt was dissolved and made up to 500 cc., and 6 liters were prepared. The correctness of this solution was determined as follows: 25 cc. were run out of a carefully calibrated burette and the  $\text{SO}_4$  determined by precipitation with barium chloride.

*Experiment.*—25 cc. copper sulphate precipitated with  $\text{BaCl}_2$ , and the following amounts of  $\text{SO}_4$  found:

Calculated $\text{SO}_4$ in 25 cc.	Found $\text{SO}_4$ in 25 cc.	
	1.	2.
0.5559 gms.	0.5556	0.5552

These figures show correctness of the solution used in the work on sugars.

*Rochelle Alkali Solution.*—Under this head two questions of interest arise:

- Does the purity of the Rochelle salt affect the solution?
- Is it necessary to prepare this solution fresh immediately before each analysis?

Allen, in his *Commercial Organic Analysis*, 2d edition, p. 225, has the following foot note:

“Much of the Rochelle salt of commerce is very impure. It is safest to prepare it by dissolving commercial cream of tartar in hot water, adding carbonate of sodium till the liquid remains slightly alkaline after boiling, filtering from precipitated calcium carbonate and crystallizing the Rochelle salt from the clear liquid.”

Careful experiments were made, using the commercial Rochelle salt and using the pure salt obtained after numerous crystalliza-

tions, but no difference could be observed in the use of the crude and C. P. article.

Soxhlet\* recommends that the Rochelle alkali solution be freshly prepared. Wein† follows Soxhlet, and remarks that old solutions give unreliable results, and emphasizes the fact that the solution be prepared "immediately before the carrying out of the determination," and Steiger‡, in a recent article, quotes Soxhlet, and adds that he can confirm the observation of Soxhlet. Frese-  
nius,§ however, in a foot note, remarks that he has found this to be unnecessary.

After careful observations, and many determinations, I cannot detect appreciable difference in the use of freshly prepared and old solutions, and the following titrations—a few of those made—fail to show any difference :

Alkali sol., fresh . . . . .	52	gms. NaOH to 500 cc.=	24.03	cc. dex. sol.	
" after standing 4 mo.,	52	" " "	24.08	" "	" "
" fresh . . . . .	40	" " "	23.77	" "	" "
" after standing 4 mo.,	40	" " "	23.93	" "	" "
" fresh . . . . .	70	" " "	24.93	" "	" "
" after standing 4 mo.,	70	" " "	24.93	" "	" "

*Preparation of Dextrose used in Experiments and Titration Against Fehling Solution.*—The dextrose used was prepared after the method of Soxhlet and in the following manner :

Warm in a large cylinder on the water bath a mixture of 12 liters 90% alcohol and 480 cc. fuming hydrochloric acid to 45° C., and bring in several portions with constant stirring 4 kgr. powdered cane sugar, and do not allow the temperature to rise over 50 degrees. After two hours the saccharose is dissolved and inverted, and a colorless sirup obtained. When the sirup has cooled, bring into it with constant stirring a quantity of water free dextrose and stir well from time to time. The separation of the dextrose begins after a few hours, and in twelve hours 70 to 80 per cent. of the yield has crystallized. The dextrose prepared in this way was re-crystallized many times from alcohol, and finally dried between filter paper and laying in the air. The purity of the preparation was determined with a large Landolt-

\*Jour. prakt. Chem. XXI, 29.

†Tabellen zur Quantitativen Best. der Zuckerarten, S. X.

‡Zeit. anal. Ch. 28, 445.

§Quant. Anal.

Lippich instrument, and this determination showed the preparation to be the hydrate and not the anhydride. A water determination gave the following :

1.4594 gms. substance showed loss of 0.1346 gms.  $\text{H}_2\text{O}$ .  
 $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$

<i>Calculated.</i>	<i>Found.</i>
$\text{H}_2\text{O}$ 9.08%	9.22%

The specific rotatory power was determined, using a 10 per cent. solution. The readings were made in the second and fourth quadrants, using a sodium flame and a 400 mm. tube.

5 gms. dry dextrose were dissolved in 45.9252 gms. water ; one part used for determining the specific gravity, and the other to determine the rotatory power.

$$p = 5.0000$$

$$p + q = 49.9252$$

$$S \text{ at } 20^\circ = 1.034^*$$

$$P = 10.02$$

QUADRANT II.		QUADRANT IV.	
Empty Tube. Neutral Point.	Full Tube. Neutral Point.	Empty Tube. Neutral Point.	Full Tube. Neutral Point.
179.38 degrees	159.58 degrees.	359.40 degrees.	339.56 degrees.
.34 "	.53 "	.39 "	.58 "
.35 "	.55 "	.36 "	.55 "
.38 "	.52 "	.37 "	.59 "
.34 "	.58 "	.36 "	.56 "
.37 "	.55 "	.34 "	.55 "
Mean, 179.36 "	159.55 "	359.37 "	339.56 "
Observed angle, 19.81 degrees.		19.81 degrees.	
Mean, 19.81 degrees.			

The specific rotatory power is calculated from the formula

$$(a) D = \frac{a. 100}{p. d. l.}$$

$$(a) D = \frac{19.81 \times 100}{10.02 \times 4 \times 1.034} = 47.82^\circ$$

Tollens, in his "Kurzes Handbuch der Kohlenhydrate," S. 45, gives the value of (a) D for a 10 per cent. solution as 47.92, and

\*In determining the sp. gr., a Sprengel picnometer was used, and Landolt's formula—

$$D = \left( \frac{F}{W} 0.99707 \right) + 0.0012$$

while my number is one-tenth low, yet it shows the purity of the preparation.

*Titration of a 1 per cent. Dextrose Solution against an Alkaline Copper Solution containing varying quantities of Alkali.*—Dextrose solution: 11 gms. dextrose dissolved in water and made up to one liter at 17°.5 C. The titrations were made as follows: 25 cc. copper sulphate were measured from the calibrated burette into an Erlenmeyer flask and to this 25 cc. of white solution added. The dextrose solution was added, the whole heated to the boiling point and after two minutes boiling, tested for copper. If the filtrate contains copper a new determination is made using more dextrose solution and this repeated again and again until a point is reached where there is no excess either of copper or of dextrose. In reckoning the two minutes the point is taken when bubbles appear, not in the middle only, but also on the sides of the flask. Immediately on ending this boiling a portion of the solution is filtered using Wiley's filtering tubes and tested for copper with ferrocyanide of potash. After a trial of all the ways of determining the end point in this titration, the Wiley filtering tubes gave the only sharp and satisfactory results. Repeating Soxlet's work with dextrose, while not agreeing exactly, gave numbers almost identical. Having established this point, the titrations were carried on with solutions using varying quantities of alkali and with results seen in the following tables :

	Rochelle Salt in 500 cm. Gms.	NaOH in 500 cm. Gms.	cm. 1% Dex- trose Solution used.	1 cc. Fehling = mgr. Copper.	REMARKS.
25 cm. alkali and 25 cm. copper	173	80	. .	. .	Could not deter- mine end point.
" " " "	"	70	24.93	4.987	Solution yellow, end point sharp.
" " " "	"	60	23.86	4.772	Solution yellow, end point sharp.
" " " "	"	52	24.08	4.816	Solution yellow, end point sharp.
" " " "	"	40	23.77	4.754	Sol. less yellow, end point sharp.
" " " "	"	30	24.18	4.836	Sol. slightly yel'w, end point sharp.
" " " "	"	20	24.10	4.820	Sol. slightly yel'w, end point sharp.

From an inspection of this table it will be seen that the number obtained, using 70 gms. alkali (corresponding to Allen's solution) gives very nearly the ratio 1 : 5, the old relation published by Fehling. This solution is a very satisfactory one for titrations but has no special advantage over the one of Soxhlet; and as the analytical data for a solution containing 52 gms. alkali have been so carefully obtained and used by the foremost sugar chemists in Germany, its use by American chemists cannot be too highly recommended.

For purposes of study and convenience of reference the numbers of Soxlet can be given here.

KIND OF SUGAR.	Time of Heating.	Undiluted.	Equal Bulk of $H_2O$ .	Two volumes $H_2O$ .	Three volumes $H_2O$ .	Four volumes $H_2O$ .
Dextrose . . . . .	2 min	.4750	.4825	.4880	.4920	.4940
Invert Sugar . . . . .	2	.4940	.5030	.5090	.5140	.5150
Levulose . . . . .	2	.5130	.5235	.5300	.5360	.5260
Milk Sugar . . . . .	6	.676	Not affected by dilution			.676
Galactose . . . . .	2	.511	"	"	"	.533
Maltose . . . . .	3-4	.778	"	"	"	.740

In conjunction with Dr. H. W. Wiley, work is now in progress with gravimetric methods using solutions containing 52 gms. and 120 gms. alkali. This comparison is being made for the purpose of determining the influence of large quantities of alkali, for a solution is wanted for quantitative work which shall have less action on sugars.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE. FROM H. W. WILEY.]

### XIII. PRESERVATION AND ANALYSIS OF SUGAR SOLUTIONS.

BY. HUBERT EDSON.

In 1871, C. Houghton Gill\* pointed out the presence of an error in the examination of low grade sugars and molasses due to the

\*Journal of the Chemical Society, 1871.

compound formed by the invert sugar with basic lead acetate. To illustrate the amount of this error some of his experiments are given below :

15 cc. of a solution of invert sugar made up to 50 cc. by water	}	Read —28.25 at 24° C.
15 cc. of same solution with water and 2 cc. of saturated solution of basic lead acetate to 50 cc.		
15 cc. of same solution with basic lead acetate solution alone to 50 cc.	}	Read +57 at 25° C.

This alteration of the rotatory power affects only the levulose of the solution, the dextrose retaining its normal effect on the polarized ray.

A solution of nearly pure levulose, prepared by Dubrunfaut's method, and reading —44 at 20° C. made up to two vols. by solution of basic lead acetate	}	Read —6 at 20° C.
A solution of pure dextrose, prepared from invert sugar, and reading 60.3, made up to two vols. by strong solution of basic lead acetate		

Gill corrected this optical error by the addition of a solution of sulphur dioxide to acidity thus breaking up the levulose compound which cannot exist in an acid solution.

These experiments were overlooked by sugar chemists for several years, the use of basic lead acetate being continued as a clarifying agent without acidifying the solution to destroy the levulose compound. Last year, however, Mr. G. L. Spencer of the U. S. Department of Agriculture, recalled attention to them and also made many experiments himself which corroborated the results of Gill in almost every particular, he using acetic acid to acidify the solution instead of sulphur dioxide. Mr. Spencer secured very accurate polariscope work and developed a method of analysis which has proved to be of great value in examinations of raw sugars and molasses.

Besides being used as a clarifying agent, basic acetate of lead is also used as a preservative of sugar solutions. This is done mostly where raw juices are worked and where there is not time to analyze samples immediately on coming into the laboratory. From solutions preserved in this way both sucrose and invert sugar are to be determined. It was from certain peculiarities in the amount of invert sugar secured that led me, last winter on

Calumet Sugar Plantation, La., to investigate as thoroughly as I could, with the apparatus there, the effect of basic lead acetate on a solution in which invert sugar is to be determined and I am now prepared to state the results are unreliable. Below are some of the representative analyses I have made on the work :

	GLUCOSE.		
	Basic Lead Acetate Added.	Basic Lead Acetate and Acetic Acid added.	No Lead or Acetic Acid added.
Clarified juice . . . . .	0.92	1.13	1.17
Sirup . . . . .	2.99	3.49	3.76
First Masse cuite . . . . .	5.66	6.71	6.91
“ “ . . . . .	5.47	6.50	6.35
“ “ . . . . .	6.39	6.25	7.04
Second “ . . . . .	11.67	13.72	14.06
“ “ . . . . .	14.86	17.73	17.29
“ “ . . . . .	13.56	14.54	15.65
“ “ . . . . .	13.54	15.21	15.47
“ “ . . . . .	12.97	15.31	15.82
Final molasses . . . . .	17.54	20.15	20.93
“ “ . . . . .	17.28	18.76	20.56
“ “ . . . . .	16.87	19.04	20.45

These analyses were made with the greatest possible care, and yet it is seen that no regularity even exists in the results. The method pursued in the examination was as follows :

Three samples were weighed out, care being taken to have the same amount in each case. To the first was added basic lead acetate solution, made up to known volume, filtered, and aliquot portion taken, excess of lead precipitated, solution made up to known volume, filtered and reducing sugars determined by Violette's modification of Fehling's solution.

To the second sample basic lead acetate and acetic acid to acidity were added, solution made up as in the first, lead precipitated, solution neutralized and diluted to same volume as first, and reducing sugars determined.



The third sample had no lead or acetic acid added but was made up to the volume in the same manner as the other samples.

This last was taken as the standard and the others compared with it. The first method gives an enormous error, amounting to about 20 per cent. of the reducing sugars present. Much work, especially in sugar houses, has in the past been done by this method and consequently is useless in comparison with results now obtained, though fortunately, such results are fairly comparable with each other.

The second method, in which acetic acid is added to the solution after the basic lead acetate, is much nearer correct. The main difficulty with it is its unreliability, the results sometimes being too high and then again too low. They are in the main too low by from eight to two-tenths of one per cent. in samples containing comparatively large amounts of reducing sugars, and nearer the low error in samples containing a small amount of these sugars. Accurate determinations of reducing sugars cannot be secured from either of the above methods.

Having proved the existence of an error when basic lead acetate was used, it became necessary to find some other reagent to take its place. The idea in adding acetic acid to basic lead acetate solution was, of course, to convert the lead oxide combined with the levulose into an acetate and leave the levulose in solution uncombined. Now when in the end this has to be done there is no reason why the normal acetate should not be used in the first place, as the lead, in combining with the impurities present in a sugar solution, frees enough acetic acid to prevent the levulose compound being formed.

There were three essential things which the normal lead acetate had to accomplish to fill the requirements of sugar work. These were a good clarification, preservation of juices, and non-interference with correct analytical results. In the first of these it is most defective, but serves equally as well as the basic acetate after acetic acid has been added to the solution; and as nothing approximating accurate results can be secured by the latter without the use of acetic acid, the two are on an equality at this point.

In regard to the preservation of juices unaltered, I measured out duplicate samples of a juice the per cent. solids of which was

15, added normal lead acetate to each, determined the reducing sugars in one immediately and allowed the other to stand one hundred hours before the determination was made. In the first 1.124 per cent. of reducing sugars were found and in the second 1.120 or a difference of only four one thousandths of one per cent. The polariscope reading on the same sample which was at first 24.475, average of four readings, was at the end of one hundred and forty-two hours 24.5, average of same number of readings. Reduced to percentages of sucrose these are respectively 12.238 and 12.25, a difference of twelve one-thousandths of one per cent.

As to the last requisite of the normal acetate, i. e., non-interference with analytical work, a table is given below showing its influence on the determination of reducing sugars :

	GLUCOSE.	
	Normal Lead Acetate Added.	No Lead Added.
Clarified juice . . . . .	1.15	1.17
“ “ . . . . .	1.12	1.13
Syrup . . . . .	3.76	3.79
Final molasses . . . . .	17.45	17.50
“ “ . . . . .	27.04	27.08

These samples were examined in the same manner as the basic lead acetate solutions, There is in each case a slightly less percentage of invert sugar shown in the normal lead acetate solutions than in the juice to which no lead had been added, but even in the molasses this does not in any case amount to more than five one-hundredths of one per cent., and can be entirely disregarded in most all sugar work.

There is a slight error in the polariscopic work which is corrected by the addition of a little acetic acid at the time of analysis

We can conclude then that the normal lead acetate simplifies the work and that we can insure correct determinations of invert sugar from solutions in which it has been used; a thing that cannot be done where basic lead acetate is the clarifying agent.

#### XIV. A GRAVIMETRIC METHOD FOR OBTAINING A CONSTANT RATIO OF REDUCTION OF COPPER WITH REDUCING SUGARS.

BY J. L. FUELING.

In pursuing my work on the gravimetric determination of dextrose and invert sugar with Allihn's modification of Fehling's agent, I observed that, though we have many methods for pursuing this work, no one of these gives us a reducing constant applicable to sugar solutions of all degrees of concentration. As from any one solution, it is, therefore, impossible to say what constant is, as the ratio of reduction is never the same with solutions containing different weights of a reducing sugar. As an example, take the results found by Allihn. A water solution of dextrose, containing 244 mg. of dextrose in 100 cc., 30 cc. of which yielded 10.0 mg. of copper, giving a ratio of 1 : 1.639. Another solution containing 805.6 mg. of dextrose per 100 cc. yielded 38 mg. of copper giving a ratio of 1 : 1.886, which shows us conclusively, that, to use Allihn's method, we must have a constant for every milligram of reducing sugar used, necessitating the use of Allihn's table of constants at all times; and this is the case with all the methods proposed. What is desired is a method which will not only give a constant with one solution, but with all solutions. In my preliminary work in this direction, I found great difficulty in obtaining duplicates which agreed by using the Sachsse method of reducing the cuprous oxide in the glass filter tube, often requiring as many as six determinations before they were found to agree. To overcome this, I prepared and used the following method:

After the copper is reduced by the reducing sugar, in the usual manner, decant the supernatant liquid into a Gooch crucible, properly mounted in the neck of a bell-jar, resting on a ground glass plate, and connected with a Sprengel's vacuum pump to assist filtration; the filtrate is reserved in a beaker placed under the bell jar; after which the cuprous oxide is washed by decantation with 100 cc. of boiling distilled water in two portions of 50 cc. each. The

beaker containing the filtrate, is removed, and the beaker containing the cuprous oxide set in its place. The cuprous oxide contained in the Gooch crucible is now dissolved with a fine stream of nitric acid, the solution of which is received in the before mentioned beaker. After removing all traces of the copper nitrate from the Gooch, with distilled water, carefully transfer the copper-nitrate solution to a tared platinum evaporating dish, add a few cc. of concentrated sulphuric acid and evaporate to partial dryness, on a steam bath, or until all of the nitric acid is removed; after which partially fill the dish with distilled water and precipitate the copper, as a bright metallic film on the sides of the dish. With ordinary care, I rarely found it necessary to make more than one set of duplicates, as the results were almost identical in the majority of cases.

I now found it a simple matter to obtain the same result as often as desired, by carefully following the same method for each, which convinced me that the entire problem was one of conditions and proportions; and, with this conclusion, I proceeded to prove my theory, with results that fully carried out my original conclusion, making it now possible to obtain a constant which will hold good in all cases, not forgetting that this constant may be any of the factors, within certain bounds, that may be decided on, as it is a simple matter to obtain a number of different weights of copper by varying the conditions and proportions in the determination.

The method and proportions used in finding the constant were as follows:

Into a beaker of about 300 cc. capacity, place 25 cc. of copper sulphate solution, 25 cc. of alkali solution and 50 cc. of distilled water, and bring to a brisk boil; into the hot solution carefully run from a burette 25 cc. of a dextrose solution, containing 990 mg. of anhydrous dextrose per 100 cc; once more bring to a boil and continue the boiling for exactly two minutes; after which filter and treat as before, care being taken to keep the cuprous oxide covered by the liquid to prevent the action of the air. After all the copper is precipitated by the electric current, it is washed carefully with recently boiled and cooled distilled water, next with 95 % alcohol, and finally with absolute alcohol. The platinum

dish is now placed on an iron or tile plate and a lighted taper applied to the adhering alcohol. As soon as this is removed, place the dish in a desiccator, after which it can be weighed.

By always observing the proportions given in the above method there is no difficulty in obtaining results which have the same constant with all solutions. As an example : For every cc. of a 1 per cent dextrose solution is required 1 cc. of copper solution, 1 cc of alkali and 2 cc. of distilled water ; or, should the solution have only .5 of a per cent. of dextrose, there would be required .5 of a cc. of copper solution, .5 of a cc. of alkali solution and 1 cc. of water ; increasing and diminishing the solutions as the sugar increases or diminishes in density. Following I give a few results obtained by myself with dextrose (anhydride) :

Sugar Solution. cc. taken.	Wt. of Dextrose. Contained mg.	Wt. of Copper. Found mg.	Ratio of Sugar. Copper.	
25	247.5	426.3	1	1.722
25	198.0	342.1	1	1.722
25	148.5	255.3	1	1.719
25	99.0	170.75	1	1.724

Mean . . . . . 1.7217  
Dextrose factor . . . . . 0.5808

Sugar Solution. cc. taken.	Wt. of Invert Sugar mg.	Wt. of Copper found mg.	Ratio of Sugar. Copper.	
25	247.57	434.5	1	1.755
25	198.0	348.3	1	1.758
25	148.5	260.9	1	1.756
25	99.0	174.4	1	1.761

Mean ratio . . . . . 1 : 1.755  
Sugar factor . . . . . 0.5698

Following I give the weights and ratios found by other chemists by their respective methods :

*Allihn's Dextrose.*

Wt. Dextrose mg.	Wt. Copper mg.	Ratio.	
247.5	459.0	1	1.854
198.0	374.0	1	1.888
148.5	285.5	1	1.923
99.0	193.5	1	1.954

*Wien's Dextrose.*

Wt. Dextrose mg.	Wt. Copper mg.	Ratio.	
252.4	470.0	I	1.862
200.5	380.0	I	1.895
150.0	290.0	I	1.933
99.1	195.0	I	1.966

*Meissl's Invert Sugar.*

Wt. Invert Sugar mg.	Wt. Copper mg.	Ratio.	
246.3	430.0	I	1.741
200.4	361.0	I	1.796
150.1	277.0	I	1.845
100.1	189.0	I	1.888

The reagents used throughout my work were prepared after the formula of Allihn's as follows :

34.639 grams of  $\text{CuSO}_4 \cdot .5 \text{H}_2\text{O}$  in 500 cc. of water  
 173.0 " " Rochelle salts " " " "  
 125.0 " " Potassium hydrate " " " "

The dextrose used was taken from the sample prepared and used by Dr. B. Tollens in determining the rotatory power of the same.

The invert sugar was prepared from pure cane sugar, polarizing 99.9 per cent. pure, as follows :

4.705 gms. of sucrose is dissolved in 200 cc. of water, after which, 20 cc. of concentrated hydrochloric acid are added : it is now heated in a steam bath to  $70^\circ \text{C}$ , removed and permitted to cool slowly. When cool it is carefully neutralized with potassium carbonate and made up to a volume of 500 cc. at  $17^\circ.5 \text{C}$ .

It is my full intention and desire to apply my method to all of the reducing and reducible sugars known and find their reducing constant. Also to its application to solutions containing unknown weights of a reducing sugar, and to make such further alterations and improvements as may be necessary to give us a method fully freed from all of the objections found in the old and faulty methods.

## XV. AN IMPROVED METHOD FOR THE ESTIMATION OF THEINE IN TEAS.\*

BY G. L. SPENCER.

The estimation of theine has received considerably more attention from analysts than the value of a knowledge of its proportion in teas seems to warrant. The estimation of the percentage of theine in a tea gives little if any information in regard to the commercial value of the latter, though, in general, it may be said the high-priced teas usually contain a large proportion of this alkaloid.

Twenty-five or more methods have been devised for the estimation of theine, though it must be said the later of these methods bear a strong resemblance to one another. In the earlier methods the alkaloid was extracted from the tea leaves by means of ether or acidulated water, the extract purified, and the theine separated by crystallization from concentrated solutions, or if finally obtained in ether or chloroform solution, by the complete evaporation of solvent. The various methods differ more especially in the purification of the solutions of the alkaloid.

In the method of Blyth the alkaloid is obtained quantitatively directly from the powdered leaves and in a state of great purity, by sublimation. Some of the later methods differ from one another only in slight variations in the manipulations, the object being the reduction of the labor required.

Weyrich (*Ztschr. anal. Chem.* **12**, 104) examined a number of theine methods and rejected all but that of Mulder. His objections to the various methods were based upon either imperfect extraction of the alkaloid, imperfect precipitation, or an impure product. The method of Mulder, which he adopted, consists in evaporating a definite volume of a water extract of the tea with magnesia, to dryness; the residue is then digested two days with ether; this latter is occasionally heated and poured off into a tared flask, a fresh portion of the solvent being added. This extraction is continued as long as the

\*See this Journal, Vol. 4, part 2, April, 1890, for the method as first published.

residue yields theine. The ether solutions are united and, finally, the solvent is removed as usual by evaporation. This is a favorite one of the older methods and is given to emphasize the simplicity of manipulation required by the method, which I propose to describe below. While the method about to be described is but little shorter than some of the new methods, which it resembles, it has the advantage of very considerable accuracy. This method may be briefly described as follows :

Transfer three gms. of very finely powdered tea to a 300 cc. flask ; fill the flask with hot water nearly to the neck ; add a small fragment of tallow to prevent foaming, heat gradually to ebullition and maintain this temperature half an hour. Small particles of tea adhering to the neck of the flask should be washed down with a few drops of water. After boiling, cool and add subacetate of lead in slight excess. The amount of the reagent required may be determined by the ease with which the precipitate separates. Approximately .3 cc concentrated lead solution is required per gm. of tea. After the addition of the lead, complete the volume to 300 cc. and shake the flask to mix its contents thoroughly ; filter off 100 cc. of the solution into a sugar flask, i. e., a flask graduated to 100 and 110 cc ; precipitate the excess of lead with hydrosulphuric acid, employing ether to prevent foaming ; heat to expel excess of the reagent, cool and complete the volume to 110 cc. The extra 10 cc. permits washing the gas delivery tube. Filter, transfer 55 cc. of the filtrate, corresponding to .5 gm. of tea, to a separatory funnel and extract seven times with chloroform. The chloroform solution of the theine is collected in a tared flask and the solvent removed by distillation and drying. The temperature at which the latter is accomplished should not exceed 79° C. The theine obtained is very pure and contains one molecule of water of crystallization.

It may be noticed in the above method that all washings of precipitates is avoided. A slight error is introduced through the non-removal of the tea residue and the lead precipitate, but this will rarely if ever exceed about .02 per cent. A second error results from leaving the lead sulphide in the sugar flask but this is extremely small, if care has been taken in adding the lead subacetate. If preferred, the lead may be removed without the use of the



sugar flask a definite volume of the solution being taken for this purpose. In this case the precipitate requires washing. It is preferable to follow the method as first described as in this way the volume of the solution in the funnel will not exceed 55 cc., a large volume being objectionable through the possibility of a portion of the alkaloid remaining in water solution.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE. FROM H. W. WILEY.]

## XVI. ON THE METHODS OF ESTIMATION OF THE FATTY BODIES IN VEGETABLE ORGANISMS.

BY WALTER MAXWELL.

These investigations have been conducted with the purpose of acquiring some further data showing the comparative proportions of matters which become separated from vegetable organisms by extracting with pure ether in variable durations of time. It has further been attempted to determine whether the whole of the substituted glycerides, or lecithines, do become separated by direct extraction with ether only.

The materials used in the work were pulverized to the greatest state of fineness, and the extractions were made with the Knorr extraction apparatus. The calculations are reduced to the standard of water-free material.

a. The preliminary experiments, which were made in order to establish the proportions of the vegetable matters separated by the action of pure ether in different durations of time, are illustrated by the following results :

Cottonseed Time	Wt. of Material Gms.	Wt. of Extract Gms.	Per Cent.
8½ hrs.	4	1.472	37.39
10 "	4	1.491	37.87
15 "	4	1.511	38.38

These results give the average of a great number of analyses. Although an increase of substance becomes separated with an increased duration of the period of extraction, the proportion is small ; and it is not apparent that the greater duration of time causes an increase in the fatty bodies only, as other matters can be affected by a very protracted boiling. For these reasons it has

been resolved to estimate the amounts of the fatty bodies separated by extraction with pure ether in a duration of 15 hours.

In considering the estimation of the proportion of glycerides and substituted glycerides, which are contained in the ether extract, the presence of other bodies, which have been removed with the ether, make it impossible, in the absence of an absolute analysis of the extract, to determine accurately the comparative relations of those fatty bodies. The ether extractions of plant matters contain variable proportions of cholesterin and of, in some instances, solid hydrocarbons, which may constitute several per cent. of the extract. However, although the percentage of glycerides cannot be definitely estimated, the lecithines or substituted glycerides, may be determined with absolute accuracy, as the estimation of these bodies rests upon the proportion of phosphorus present in the ether extract. The extract is ignited with mixed alkali salts by which the phosphorus present in the organic form as lecithine becomes fixed as an alkali phosphate and is then determined as magnesium pyrophosphate, and the latter body being multiplied with the known Hoppe-Seyler factor, gives the exact amount of lecithine.

A further series of extractions was made of the pulverized cottonseed with pure ether for a period of 15 hours and the total extract determined. The proportion of lecithine contained in the extract was estimated by the method already given, the residue of the extract being considered as glycerides and other bodies. The average of eight analyses gave the following results ;

Per Cent. of Extract . . . . .	38.46
Per Cent. Glycerides etc. . . . .	98.84
Per Cent. Lecithines . . . . .	1.16

*b.* It will be shown that the proportion of substituted glycerides stated, 1.16 per cent., does not represent the total lecithines present in the cottonseed.

The observation was made simultaneously by Prof. E. Shulze, Zurich, and W. Maxwell, of Harvard College, that the substituted glycerides do not become wholly separated by extraction with ether, even in a great duration of time. It was found that if the material which had been already extracted with ether, were further extracted with absolute alcohol another portion of substituted gly-

cerides was obtained, which, in most instances, was greater than the amount separated by the ether. The process of the alcohol extraction consisted in merely extracting the material already treated with ether and evaporating off the alcohol, and re-extracting the alcohol extract residue with ether. The reason for taking up the lecithines out of the alcohol extract was that it has been observed that those lecithines which were originally insoluble in ether, became soluble in that menstruum when previously acted upon by alcohol. The use of ether was further made to avoid any small portion of inorganic phosphates which might have been removed from the vegetable material by alcohol. It was found, however, that only a mere trace of mineral phosphates had been separated by the action of the alcohol.

The amount of the ether extraction of the alcohol extract in 100 parts of the vegetable material with the proportion of lecithines was as follows :

Extract . . . . .	2.3 %
Lecithines in extract . . . . .	16.6 "

A further comparison indicates the following :

	Extract	Lecithines	Glycerides etc.
	%	%	%
Ether . . . . .	38.46	1.16	98.84
Ether and alcohol . . . . .	40.76	2.30	97.69

The proportion of lecithines to the total fatty bodies contained in the cottonseed is very small, yet it is seen that about 50 per cent. of those substituted glycerides are left in the material after extraction with ether for a period of 15 hours. If certain other varieties of seeds be considered, such as the legumes, pea, vetch, bean, Boston bean, etc., it is found that the total ether and alcohol extracts of those seeds are composed of lecithines varying from 25 to 45 per cent. It is thus apparent that, in the examples of seeds given, as far as 20 per cent. to 25 per cent. of the total fatty bodies can remain unseparated and undetermined when the material is extracted with ether only.

# ON THE DETERMINATION OF AVAILABLE PHOSPHORIC ACID IN FERTILIZERS CONTAINING COTTON-SEED MEAL.\*

BY F. B. DANCY, A. B.

The term *available* phosphoric acid is used to denote the difference between the *total* phosphoric acid in a fertilizer and the *insoluble*. The total phosphoric acid is the entire amount of phosphoric acid, of whatever kind, that the fertilizer contains. The *insoluble* phosphoric acid is, as generally accepted, that phosphoric acid which is left after two grams of the fertilizer, ground to pass a sieve of approximately twenty meshes to the linear inch, have had the *soluble* phosphoric acid extracted with cold water and then been digested for thirty minutes, with agitation every five minutes, at 65° C., with one hundred cubic centimeters of a strictly neutral solution of ammonium citrate of a specific gravity of 1.09, immediately after which digestion they have been thoroughly washed with cold water.

The *available*, then, being the difference between the *total* and the *insoluble*, it follows that *insolubles* being equal, the *available* varies exactly and directly as the *total*; and *totals* being equal, the *available* varies exactly, though inversely, as the *insoluble*.

The *total* is a definite and fixed quantity, and there should, therefore, be no material variation in its determination between the work of accurate analysts. Not so with the others. The *soluble*, *insoluble*, *reverted* and *available*, are not fixed and definite quantities. They are dependent on so many conditions of time, temperature, degree of fineness, quality and quantity of solvent, agitation, etc., that it is no matter of wonder that even skillful manipulators vary in their determination. They are the results of methods, and will vary according to the method or the manner of executing the details of the method. But, as has been remarked and as its name implies, the *total* is *all* the phosphoric acid in the material under examination, of whatever kind and in whatever shape or form. It is not what is gotten by a method but *what*

\*This paper was submitted to the meeting of the Association of Official Agricultural Chemists which convened in Washington in August last, and, upon the recommendation of the Reporter on Phosphoric Acid Determinations, the convention voted unanimously to condemn methods Nos. 2 and 3, where fertilizers containing cotton-seed meal were to be analyzed, and to use only method No. 1.

*there is there*, and any method, therefore, that fails to reach any part or kind of it, is not a method for *total* phosphoric acid. It is sometimes said that discrimination is impracticable, and that all fertilizers should be treated equally and alike. The position is untenable. It might as well be urged that in order not to discriminate, the plain soda-lime method for the determination of nitrogen should be used on all fertilizers, those containing nitrates as well as those containing organic nitrogen alone, when every one knows that it is inadequate in the presence of nitrates. So a *total* method which is adequate for some kinds of fertilizers but not for others cannot be applied to all on the above ground or any other ground, without manifest injustice to those fertilizers for which the method is inadequate.

The Association of Official Agricultural Chemists in their official methods (Bulletin 24, United States Department of Agriculture), give three alternate methods of determining *total* phosphoric acid. There is no distinction made between them, no indication that either is better adapted than the other for any particular class of fertilizers. The presumption is, that they are given as interchangeable and equally allowable for all classes of fertilizers, at the pleasure or option of the operator. It is the purpose of this article to show that one of them, at least, is entirely inadequate for fertilizers that contain cotton-seed meal, and that any chemist who uses this method on such fertilizers is in almost certain danger of doing these fertilizers a great injustice. The method referred to is the second of the three given, namely: "Solution in thirty cc. of concentrated nitric acid with a small quantity of hydrochloric acid." The writer has not extended his investigation, except imperfectly, to the other two methods. It is only with this one, as applied to cotton-seed fertilizers, that this article has to do.

Cotton-seed fertilizers are comparatively unknown in the North. It seems, therefore, that the Southern members of the A. O. A. C. must not have been very wide awake to the interests of a class of fertilizer manufacturers peculiar to their own section of country when they failed to have attached to this method, at the time when it was adopted by their Association as one of three alternate methods, the limitation "not applicable to fertilizers containing cotton seed meal."

Cotton seed meal is readily and entirely soluble in either "nitric acid with a small quantity of hydrochloric acid" or of nitric acid alone. *But such a solution does not give up its phosphoric acid to molybdic solution.* It would appear that certain nitro-organic compounds are formed which prevent the phosphoric acid in the solution from being yielded up to the molybdic precipitant. Whether this is effected by in some way rendering the menstruum a solvent for the phospho-molybdate of ammonia that ought to be formed, or, by holding the phosphoric acid in check, serves thus to prevent such a combination, is not clear. But the fact remains. The attention of the writer was first forcibly directed to it when a sample of cotton seed meal was submitted to him for a determination of the *available* phosphoric acid it contained. A nitric acid solution of two gms. of it was made (using also a little hydrochloric acid), the solution being perfect, and a total phosphoric acid percentage of 0.51 found. A duplicate made in the same way yielded 0.54 per cent. Being convinced that there was much more phosphoric acid in the meal than this, and recalling that a short time previously a gentleman had remarked that a friend of his had found materially more phosphoric acid in the ash of Cotton seed meal than by acid solution, two gms. of the meal were ignited to perfect ash, the ash dissolved in acid, and a percentage of 3.24 of *total* phosphoric acid found; a duplicate in the same manner yielded 3.20, though in this case the incineration was not quite so perfect, a little char being left. The true per cent. of *total* phosphoric acid in the meal then was 3.24. A solution of two grams made by hydrochloric acid with chlorate of potash also failed by something more than half of getting the full amount. This yielded 1.45 per cent. Next two grams of the meal were taken, washed with cold water in exactly the same manner as when extracting the *soluble* phosphoric acid from an ordinary fertilizer, then digested with citrate solution and again washed exactly as is done in the determination of *insoluble* phosphoric acid. The residue was ignited and the phosphoric acid determined. It was found to be 0.24 per cent. So not only did a cotton-seed meal which showed only half a per cent. of *total* phosphoric acid to a nitric acid solution contain in reality three and a quarter per cent., but three per cent. of this three and a quarter per cent. was *available* by the methods of analysis.

A cotton-seed meal fertilizer may easily contain one-third cotton-seed meal, and, if the meal had the composition of that examined above, would owe one per cent. of its *available* phosphoric acid to the meal, if, therefore, such a fertilizer were to be analyzed by the nitric acid method, it would theoretically show a shortage of nearly one per cent. of *available* phosphoric acid (0.90 exactly). While none of the experiments herein given exhibit as great a disparity as this, some approximate it, and it is believed that a disparity fully equal to this is quite possible. Whether the entire disparity is always due to the retention of the phosphoric acid of the meal alone, or whether in some cases the meal, while holding some of the phosphoric acid of the phosphate in check, gives up more of its own, or whether, in other cases, the phosphoric acid of the phosphate in precipitating carries more of the meal's phosphoric acid down with it, than would otherwise go, and thus lessens the disparity, is not clear. I am inclined to think that new and fresh meal will exhibit this peculiarity in a greater degree than old meal, though of that I cannot speak definitely. However that may be, there seems to be not much doubt that the disparity will be greater or less, according to various conditions not well understood, and may vary from a third or a half of a per cent. to even as much as one per cent.

Six fertilizers containing cotton-seed meal were chosen. They were not laboratory mixtures, but *bona fide* commercial fertilizers on sale in North Carolina. They will be distinguished as 56, 76, 77, 78, 110 and 57. In each the phosphoric acid was determined by dissolving two grams in nitric acid plus a little hydrochloric acid with protracted heating. This is designated in the table below as "acid solution." Then in each the phosphoric acid was determined by incinerating two grams and dissolving the ash in nitric acid. This is designated in the table as "incineration." Following are the results :

Total Phos. Acid . .	56	76	77	78	110	57
Incineration . . . .	10.04	9.77	9.16	9.93	10.07	9.97
Acid Solution . . . .	9.49	9.13	8.66	9.25	9.56	9.95
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
Difference . . . .	.55	.64	.50	.68	.51	.02

No. 57 was an old cotton-seed meal fertilizer that had been

carried over from last season. The meal had completely changed color to a dark brown, so that to the eye the fertilizer would never have been judged to be a cotton seed fertilizer. In this one alone was there no difference in the results of the two methods.

It is believed that the disparity in all these cases is probably not so great as it should be ; that is to say, that the incineration method as here used probably does not give the full content of phosphoric acid, for this reason. The inferiority of the solvent power of nitric acid for phosphates to that of hydrochloric acid is well recognized. I believe that this inferiority is greater when the phosphate has been ignited. To test this, an acid phosphate was chosen, of which two grams were dissolved in nitric acid and hydrochloric acid, and the total phosphoric acid found to be 14.56 per cent. Another two grams were then ignited for about the same length of time that it requires to incinerate two grams of a cotton-seed meal fertilizer to complete ash, and then dissolved in nitric acid. The determinations were parallel, so that each received the same amount of heating with acid, which was protracted. In the case of the ignited phosphate, undissolved portions were plainly manifest to the eye, and the percentage found was only 13.62. The undissolved portions were filtered out, and readily yielded to hydrochloric acid, giving a fulsome precipitate of phosphoric acid. Next, another two grams were ignited and dissolved in hydrochloric acid, when the full content of phosphoric acid was readily yielded. Hence, it is concluded, that had hydrochloric acid been used to dissolve the six incinerated fertilizers employed in the above experiments, higher percentages would in all probability have been found. Fusion would have furnished an absolutely certain means of arriving at the undoubted maximum content of phosphoric acid, but time was limited, and simple incineration was resorted to on account of expedition ; and solution in nitric acid instead of hydrochloric acid was employed after incineration because, as the results were to be compared, it was advisable to employ the same solvent power in each case.

In addition to the six experiments described above, attention is called to the following : Two samples of cotton-seed fertilizers were procured in which another chemist had made determinations of *total* phosphoric by the nitric acid method. His *totals* were



9.13 and 9.33. I found by incineration and solution in hydrochloric acid 9.85 and 10.13, a difference of 0.72 per cent. and 0.80 per cent. respectively. Taking his own determinations of *insoluble*, the *available* by his analysis was 0.72 per cent. short in the first instance (7.40 per cent. when it should have been 8.12 per cent.), and 0.80 per cent. short in the second instance (7.50 when it should have been 8.30 per cent.) The disparity here is excessive, but the fault is not due to the chemist, but to the method. Being one of the alternate methods of the A. O. A. C., he had no reason to doubt its adequacy.

Having looked at one side of the determination of *available* phosphoric acid in fertilizers containing cotton-seed meal, let us turn to the other, namely, the determination of *insoluble*. As almost the entire content of phosphoric acid in the meal has been shown to be available, it might be anticipated that there would probably not be much difference in the determination of *insoluble* whether the citrate-extracted residue is first incinerated or dissolved directly in acid. Such was found by experimentation to be the fact. In fact, in every case but one (and this was the same fertilizer that was the exception to the *total* rule, namely, the old one brought from the previous season), a slightly higher, *insoluble* was found by dissolving in acid directly than after incineration.

The details of the two methods of determining the *insoluble* were these: After filtering from the citrate and thoroughly washing, the filter and contents were in the first instance incinerated and the ash dissolved in nitric acid (designated in the table below as "incineration"), and in the second instance the filter and contents were introduced directly into flasks and completely dissolved with nitric acid and a little hydrochloric acid (the "acid solution" of the table below). The samples used were the same as those used in the total experiments, with the exception of 110, which was not used.

Insoluble Phosphoric Acid . . .	56	76	77	78	57
Incineration . . . . .	0.84	1.80	0.86	0.87	1.59
Acid Solution . . . . .	1.00	1.91	1.28	1.05	1.42
Difference . . . . .	.16	.11	.42	.18	. .

Whether the excess of *insoluble* by direct acid solution was due

to mechanical loss in the incineration by the other method (which in these instances is not at all apprehended, though it is believed that care is necessary to with certainty guard against such loss), or whether, as is much more likely, it was due to imperfect solution of the ignited phosphate by nitric acid (a danger already pointed out), is not positively shown. But it should be remarked that in the case of 77, which is the case of greatest disparity, the undissolved portions were manifest to the eye, and it is the writer's conviction that had hydrochloric acid been used instead of nitric there would have been no material difference in the results of the two methods, either in these particular determinations, or in any other determinations. It is regarded as certain, therefore, that there will be found no material difference in the *insoluble* by which ever way determined. This being true, the *available* will vary directly and exactly as the *total*; and, therefore, by just so much as a *total* is short on account of the inadequacy of the nitric acid method when used on cotton-seed meal fertilizers, by just so much will the *available* be short.

Now a few words as to what method *is* adequate and a very few experimental determinations on this point, and the subject will for the present be laid aside. It is a matter of regret to the writer that the time was not at his disposal for more extended experimentation on the subject. Nevertheless he is none the less convinced, on account of the limited number of experiments here presented, of the truth of the point urged.

In order to compare the *total* as made by several different methods sample 110 was chosen. This sample was sent by a fertilizer company who took a fair sample of a large lot of goods at their factory, thoroughly mixed the sample and sent one-half to the writer and one-half to a chemist in another State. The *total* was determined first by fusing two gms. of the fertilizer with a mixture of equal parts of carbonate of soda and nitrate of potash, as giving with certainty the maximum content, and furnishing a standard for comparison. It was then determined by incineration and solution in hydrochloric acid, by incineration and solution in nitric acid, by solution direct in hydrochloric acid with chlorate of potash, and lastly, by solution direct in nitric acid and a little hydrochloric acid. Following are the results :

Fusion, . . . . .	10.14 per cent.
Incineration and solution in HCl. . . . .	10.09 "
"      "      "      HNO <sub>3</sub> . . . . .	10.07 "
Solution direct in HCl. + KClO <sub>3</sub> . . . . .	10.11 "
"      "      HNO <sub>3</sub> + little HCl. . . . .	9.56 "

From the above it seems that in this case all the methods save the nitric acid method were adequate, but it is not apprehended that this will hold good in all cases. For, while here incineration and solution in nitric acid sufficed, there is certainly the danger of imperfect solution already referred to; and while here also solution in hydrochloric acid with potassium chlorate sufficed, it has already been shown that this method failed to extract, from the meal alone, more than half its contents of phosphoric acid. Fusion is, of course, always adequate, but too time-consuming, if any other adequate method less so is at hand. It seems probable that incineration and solution in hydrochloric acid furnishes all that could be desired.

It is in point to add that in this case the writer reported to the manufacturers a *total* of 10.11 per cent., this being an average of the first four determinations. The *insoluble* found by incineration and solution in hydrochloric acid was 1.47, making an *available* of 8.64. It is not known what method the chemists used to which the other half of this sample was sent, but his *total* was 9.72, his *insoluble* 1.50 and his *available*, therefore, 8.22. Note that the two *insolubles* are practically the same, and that, therefore, his *available* is less than the writer's by practically the same amount that the writer's *total* is greater than his.

ANALYTICAL LABORATORY,  
133½ FAYETTEVILLE ST., RALEIGH, N. C.  
March 18, 1890.

# INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL.\*

EXTRACTS FROM THE WORK OF THE AMERICAN COMMITTEE.  
BY JOHN W. LANGLEY.

In the summer of 1888 it was the fortune of the writer to present the subject of the desirability of establishing a set of samples of steel, which should be analyzed with extreme care, in order that they might become standards to which scientific and commercial analysis of iron and steel could be subsequently referred. Also, that greater uniformity in the results of analyses might be brought about, since these standards would bear towards analytical methods somewhat the position which the original units of weight and length, the gramme and meter, or the pound and yard, preserved in Paris, London and Washington, do the mechanical arts.

The plan met with hearty coöperation, with the result that committees were appointed in Sweden, Germany, France, England and America to receive the material and to see that the necessary analyses were executed.

In England the British Association for the Advancement of Science appointed a committee, who subsequently published a plan of operations for that country, reports of which will be found in the British Association Transactions for 1888 and 1889.

The writer of this paper was entrusted with the duty of preparing the material and distributing it to the five countries named. This has been done, and analytical work on the steel is now going forward.

In the United States a committee of seven chemists was appointed to make the analyses, consisting of

Andrew A. Blair . . . . .	Philadelphia, Pa.
Regis Chauvenet . . . . .	Golden, Colorado.
Thomas M. Drown . . . . .	Boston, Mass.
Chas. B. Dudley . . . . .	Altoona, Pa.
John W. Langley . . . . .	Pittsburgh, Pa.
Albert B. Prescott . . . . .	Ann Arbor, Mich.
Porter W. Shimer . . . . .	Easton, Pa.

\*Read at the Joint Session of English, German and American Mining Engineers, at Pittsburgh, October, 1890.

This committee held a meeting at Washington, Feb. 19th, 1890, and came to the decision that the whole subject of the existing methods for the determination of carbon in iron and steel seemed to be affected by so many discrepancies and differences of opinion that, before beginning work on the International Standards, it would be desirable to make a preliminary study of methods. Accordingly, the writer was asked to prepare some additional material which could be used in somewhat large quantities for the above purpose only, and which should be known as the "Experimental Standards," to distinguish them from the "International" ones.

#### METHOD OF MAKING THE EXPERIMENTAL STANDARDS.

An ingot of tool steel,  $3\frac{1}{2}$  inches square, poured from a single crucible in which the metal had been thoroughly "dead melted," was heated and hammered barely enough to round off the corners. The ingot was then cut into two pieces, one of which was then reheated and hammered down to a bar  $1\frac{1}{2} \times \frac{3}{4}$  inches. The other half of the ingot was turned in a lathe with a blunt tool, exactly as in the manufacture of the International Standards, and the turnings, after sifting from fine dust, were thoroughly mixed and then sealed up in glass jars. The hammered bar was drilled and the drillings similarly treated. This material was given by the Crescent Steel Company, of Pittsburgh.

The object of this was to have two bodies of metal presumably identical in original composition, but one of which had received a large amount of mechanical work, the other approximately none. These samples are designated Exp. Standard, Ingot, and Exp. Standard, Hammered, respectively.

#### SCOPE OF THE PROPOSED WORK.

The Committee decided to limit the investigation to the following points at first:

- a. The best method of conducting the igneous combustion of the carbon previously liberated from the metal by a solvent.
- b. The best method of conducting the aqueous combustion of the carbonaceous residuum left by the solvent.
- c. The influence of the solvent on the quantity and mode of release of the carbon.

For division *a* it was decided further to commence with a study of the method of burning the carbon in a stream of oxygen.

This work was assigned to Messrs. Blair, Dudley and Shimer.

For *b*. The examination of oxidation methods by hot solutions of sulphuric and chromic acids. Work by Mr. Langley.

For *c*. The use of a double chloride of copper and ammonium, or of copper and potassium, either neutral or acid. Work by Messrs. Blair and Dudley.

A description of the apparatus for igneous combustions is as follows :

The apparatus used by Dudley, consisted of an ordinary Bunsen furnace with 15 burners, in which was a porcelain combustion tube five-eighths of an inch internal diameter, and eighteen inches long. Inside this tube, about three inches from the end toward the absorption apparatus, was granulated and porous oxide of copper, occupying about four inches of the length of the tube, and filling the bore. This was held in place by asbestos plugs at either end. Next to the oxide of copper, toward the boat, was placed a roll of metallic silver about 4 inches long, nearly filling the bore of the tube. Rubber corks were used at each end. The combustions were all made in oxygen gas, using air to finish the aspiration and clean out the tube. The oxygen gas used was obtained in the market in cylinders, the gas being compressed to 250 lbs. per square inch. Between the oxygen holder and the combustion tube was placed, first, a copper tube, about four feet long, and  $\frac{1}{4}$  inch in diameter, fitted with three coils at the middle ; next a potash bulb, and after that a chloride of calcium tube. All the oxygen gas, and the air used in the combustions, was passed through these parts. The copper coils were kept red hot by a Bunsen burner, during the passage of the gases, the idea being to burn any possible traces of combustible in the gas or air, and absorb the  $\text{CO}_2$  formed before they should go into the combustion tube. Between the absorption end of the combustion tube and the potash bulbs were, first, a washing tube containing about 5 cc. of sulphate of silver solution with perhaps  $\frac{1}{2}$  a gram. of silver sulphate, and next, a chloride of calcium tube. The potash bulbs were of the Geissler form, of small size, made to order. These were fitted with a small chloride of calcium tube containing chlo-

ride of calcium simply, and commonly called the prolong. The whole absorption apparatus weighed, when charged, about 60 grams. The absorbing solution in the bulbs was the ordinary caustic potash solution recommended by Fresenius. The absorption apparatus was protected against the aspirator bottle by a full size chloride of calcium tube. The joints were made with ordinary rubber tubing. The carbon from the steel was caught on an asbestos filter in a platinum boat, and dried after very complete washing at about  $90^{\circ}\text{C}$ . The boat with its filter and carbon was put into the tubes without transfer. During combustion a slight pressure above the atmosphere was always maintained in the combustion tube. Careful experiments show that the sulphate of silver washing tube is a complete protection against hydrochloric acid, and the metallic silver in the tube was relied on for protection against free chlorine, or other chlorine compounds. The time of making a combustion was about an hour and a quarter; fifteen to twenty minutes being taken to heat the oxide of copper, about half an hour for the burning, and twenty-five to thirty minutes for the air aspiration. Blair's apparatus is substantially the same as the above. His purifying train following the combustion tube contains a tube of anhydrous sulphate of copper on pumice stone. This tube is always freshly filled.

Shimer's apparatus is a porcelain tube containing oxide of copper. A stream of purified oxygen is used. An anhydrous copper sulphate absorbing tube is employed, and then the customary  $\text{CaCl}_2$ ,  $\text{KHO}$ , and  $\text{CaCl}_2$  absorbents.

#### PRELIMINARY RESULTS OF OXYGEN COMBUSTION.

In the following analysis, a solution of double chloride of copper and ammonium, except where otherwise noted, was used as the solvent of the steel. The carbon sponge was washed with dilute  $\text{HCl}$  and water till the filtrate was free from chlorine, then the asbestos with adhering carbon was put into the combustion tube. These determinations were made before the elements of uncertainty attaching to the use of double chloride were discovered, and it will be seen in the latter part of this paper, that quite different numbers can be obtained.

Under date of April 22d, 1890, Dudley reports: Exp. Standard, Ingot, contains—

Carbon	1.058 per cent.
"	1.065 "
"	1.052 "
"	1.058 "
<hr/>	
Average	1.058 per cent.

Ditto Hammered Standard :

Carbon	1.050 per cent.
"	1.051 "
"	1.051 "
"	1.060 "
"	1.050 "
"	1.056 "
"	1.056 "
<hr/>	
Average,	1.053 per cent.

Under date of April 5th, 1890, Blair reports, that using double chloride of copper and ammonium, with enough ammonia added to produce a slight cloud, and redissolving the basic salts formed in acidulated double chloride, he obtains :

	INGOT.	HAMMERED.
Carbon	1.016	1.022 per cent.
"	1.013	1.020 "
"	1.015	1.025 "
"	1.010	1.022 "

He then weighed out four portions of the "Ingot" sample, and added to each 200 cc. double chloride of copper and ammonium, after adding to each the following amounts of strong HCl :

HCL.	CARBON.
10 cc.	1.048 per cent.
20 "	1.048 "
30 "	1.048 "
40 "	1.051 "

He then took four portions of the "Hammered" sample, and treated them each with 200 cc. of double chloride, and 20 cc. HCl. Results :

Carbon	1.046 per cent.
"	1.046 "
"	1.044 "
"	1.049 "



Showing that the addition of HCl in excess of five per cent. does not sensibly change the results.

A combustion of sugar at the same time, showed :

Carbon . . . . .	42.05 per cent.
" . . . . .	42.14 "
Theory . . . . .	42.11 "

In answer to the suggestion that possibly oxides of nitrogen might be derived from the breaking up of ammonia retained by the carbon sponge, Blair reports, under date of April 17th, that he has made four combustions on the "Ingot" sample, using a four times recrystallized double chloride of copper and *potassium*.

No. 1, Carbon . . . . .	1.010 per cent
" 2, " . . . . .	1.044 per cent
" 3, " . . . . .	1.012 per cent
" 4, " . . . . .	1.022 per cent

No. 1 was dissolved in the filtered solution of the above double chloride.

No. 2 was dissolved in 200 cc. double chloride, with 200 cc. strong HCl.

Nos. 3 and 4 were dissolved in the filtered double chloride, to which enough potassic hydrate had been added to produce a slight permanent precipitate.

Blair offers the hypothesis that a strictly neutral or slightly alkaline double chloride dissolves a small portion of the carbonaceous matter, which is consequently lost so far as the combustion is concerned. Therefore, the addition of acid, by preventing this action of the liquid on the carbon sponge, will give higher and more nearly accurate results.

That the use of an acid double chloride solution gives higher results was promptly verified by Dudley and Langley. This subject is more fully discussed in the latter portion of this paper.

Shimer reports, April 25th, that by using four gms. of steel in a neutral solution of double chloride of copper and ammonium, he obtains :

"Ingot," average of two combustions, 1.055 per cent.

"Hammered," average of two combustions, 1.052 per cent.

#### THE WET METHOD.

The chromic acid combustion was conducted in an apparatus

originally designed by Dr. Herman Wedding, although the method of absorption used by him has been radically modified. Wedding's design consists of a flask capable of holding 220 cc. and provided with a glass cap of two tubulures; through one of these passes a funnel tube with stop cock, and through the other the delivery tube surrounded by a water jacket. All the joints are of ground glass.

The merit of this apparatus is its compactness and its freedom from rubber or cork joints, at least in the parts liable to come in contact with chromic acid. The absorption train, which is wholly different from Wedding's, consists of:

1st. A tube filled with pumice stone and anhydrous sulphate of copper.

2d. A small washing bottle containing the "pyro" solution referred to later on.

3d. A solution of sulphate of silver.

4th. A wash bottle of strong sulphuric acid.

5th. A chloride of calcium tube, having a small plug of moist cotton in its anterior end.

6th. A Leibig tube, containing potassic hydrate solution.

7th. A U tube, having solid potassic hydrate in its anterior limb and granulated calcium chloride in the posterior one.

8th. A chloride of calcium guard tube.

9th. An aspirator filled with water.

The absorption portion for  $\text{CO}_2$  is constituted by Nos. 6 and 7. The other parts, except Nos. 2 and 3, need no explanation, since they are well known adjuncts of the chromic acid method described in such treatises on analysis as those of Fresenius and of Blair.

The method of conducting a combustion is to place the carbon, which has been liberated from 3 gms. of steel by the action of 150 cc. of solution of double chloride of copper and ammonium, to which 10 cc. of  $\text{HCl}$  has been added, into the flask, and run in through the funnel tube 100 cc. of a solution made by dissolving 10.5 gms.  $\text{CrO}_3$  in 66 cc.  $\text{H}_2\text{O}$  and adding 210 cc. strong  $\text{H}_2\text{SO}_4$ . Purified air is drawn through at the end of the combustion.

The train as first used did not contain the "pyro" tube No. 2;

under these conditions the following numbers were obtained from the Exp. Ingot Standard :

Carbon . . . . .	1.099
" . . . . .	1.145
" . . . . .	1.040
" . . . . .	1.058
" . . . . .	1.109

A search was instituted to find the cause of these discordant results. It is well known that the carbon sponge from the action of the double chloride retains chlorine or hydrochloric acid in a form not removable by washing ; suspicion at once fell upon the HCl known to be evolved from the carbon sponge.

A series of blank combustions were made, and also mixtures of air and HCl were drawn through the absorption train. It was found that the anhydrous  $\text{CuSO}_4$  would only stop HCl when it was perfectly fresh and in relatively large quantity, a quite small degree of hydration impairing its absorbing powers seriously. A tube containing an aqueous solution of sulphate of silver was then added to the  $\text{CuSO}_4$  tube with the result that vapors of HCl are perfectly and completely arrested. When this point was established blank combustions were made and small quantities of chlorides introduced into the chromic acid mixture ; it was invariably found that the potash bulbs gained in weight. As one example out of many the following is quoted :

One-tenth gram of NaCl in generating flask.  $\text{CuSO}_4$  and  $\text{Ag}_2\text{SO}_4$  absorbents were interposed. The silver solution showed not a trace of chloride and yet the potash train gained .0055 gms.

This gain appears to be owing to chloro-chromic anhydride, or to oxides of chlorine, not absorbable by copper or silver sulphates.

This observation is not new, for it has previously been noted by other chemists that chloro-chromic anhydride was not arrested by copper sulphate.

After a long series of experiments an absorbent for these bodies has been found in the following solution :

Pyrogallic acid . . . . .	.2 gms.
Potassium oxalate . . . . .	5. "
Sodium chloride . . . . .	3. "
Sulphuric acid . . . . .	.2 "
Water to make up to . . . . .	20. cc.

The theory of the action of this mixture is as follows :

The pyrogallic and oxalic acids are deoxidants. The sulphuric acid will form potassium sulphate liberating a very little free oxalic acid to guard against the solution becoming alkaline. The sodium chloride is not essential, but it is advantageous by diminishing the solubility of  $\text{CO}_2$  in the liquid.

The action of the absorption is very energetic. It will allow  $\text{HCl}$  to pass through it without change, but the smallest traces of free chlorine, or oxides of chlorine, or of chloro-chromic anhydride, at once turn the solution brown, and are either arrested or changed into  $\text{HCl}$ . Indeed, as a qualitative reagent this liquid will approximate to iodized starch paper.

In using this in the absorbing train, the copper sulphate tube may be dispensed with, the pyrogallic liquid being used in its place, and followed by a sulphate of silver tube, so that the train between the generating flask and the potash bulbs will contain : 1 A cooling tube ; 2 The "pyro;" 3 The sulphate of silver ; 4 sulphuric acid ; 5 chloride of calcium.

Blank "combustions" were made as before with  $\text{NaCl}$  using the Pyro train till it was proved that there was no systematic gain in weight of the potash bulbs.

As examples of carbon oxidation in *presence of chlorides* : Taken .0712 gm. sugar with a crystal of  $\text{NaCl}$ . Found .1098 gm.  $\text{CO}_2$ . Theory .110 gm. Taken .030 gm. Ceylon graphite, of about 3 per cent. ash. Found .0292 carbon, equal to 97.3 per cent. carbon.

The following analyses were then made, using the new train :

Exp. Standard, Hammered . . . . .	1.075 per cent. C.
" " " . . . . .	1.070 " "
" " Ingot . . . . .	1.041 " "
" " " . . . . .	1.034 " "

It seemed possible that the carbon sponge left on the asbestos, after filtering from the double chloride solution, might suffer a slight oxidation and loss of carbon while drying. A set of duplicate analyses were therefore made on a variety of steels. The terms wet and dry, below, refer to the state of the carbon sponge when introduced into the chromic acid flask. The drying was performed at a temperature not above  $100^\circ \text{C}$ .

## CARBON IN STEEL.

		WET.	DRY.	
Steel	A	.981	.936	per cent. C.
"	B	.836	.813	"
"	C	.904	.891	"
"	D	1.054	1.073	"
"	E	1.145	1.154	"
"	F	1.095	1.108	"
"	G	1.027	.968	"
Pig		3.695	3.722	"
Totals		10.737	10.665	"
Average		1.342	1.333	"

These determinations were made before the discovery of the variability of action of double chloride with age and manner of crystallizing, to be pointed out hereafter. Moreover, they were distributed over a period of three months, so that some of the differences may be properly attributed to the chlorides used. Still, these would pretty well neutralize each other in sixteen determinations, so that the average identity of the final averages would appear to show that the sponges do not lose appreciable amounts of carbon by drying.

On the other hand, the "Hammered" Standard, similarly treated, but having the sponge dried in an air bath at a temperature not exceeding 120° C., gave,

	WET.	DRY.
Carbon . . . . .	1.064	1.027
" . . . . .	1.059	1.023
" . . . . .	1.064	1.018
" . . . . .	1.045	1.032
Average . . . . .	1.058	1.025

Apparently, therefore, there is a loss of carbon by drying the sponge at temperatures above 100° C. The same double chloride, acidulated, was used in these eight determinations.

## MODE OF RELEASE OF CARBON.

In pursuance of the special work assigned to Dudley, in a study of the phenomena attending the release of the carbon from its connection with iron in the steel, some quite surprising results have been obtained. It is, perhaps, not too much to say that sufficient work has already been done to throw doubt on the accuracy

of all recent carbon determinations made with preliminary solution of the steel in double chloride of copper and ammonium.

Dudley began his study of this problem of the release of the carbon by quite an amount of preliminary study on the reliability of his apparatus and method of making combustions. A number of modifications were tried, but finally the apparatus and method previously described under the heading, Dudley's Apparatus and Method, were settled upon, and this apparatus and method were checked up by the following determinations :

Into an ordinary glass combustion tube some 60 grams of the well known combustion mixture of chromate of lead and bichromate of potash were placed, taking care that the material did not reach to either end of the tube, and holding it in place at each end by asbestos plugs previously ignited. The tube was then placed in the furnace and a combustion made in the regular way, the position of the material, not reaching to either end, allowing the whole of it to be uniformly heated. This combustion was simply a blank to eliminate any possible error due to impurities in the combustion mixture. A small increase in weight in the absorption apparatus was found, and a second blank gave exactly the same results. This being done, three samples of three gms. each of the experimental standard ingot were treated with 200 cc. each of the same double chloride solution rendered acid by 10 cc. HCl. As this solution of double chloride will be referred to hereafter, we will say that it was made in Dudley's laboratory by obtaining from the market commercial chloride of copper and commercial chloride of ammonium, and dissolving these in water and mixing them in the proportions to form a double chloride containing one molecule each of the two salts. A small amount of free ammonia was added, enough to cause a perceptible separation of hydrated oxide of copper. The solution was then allowed to settle, and always filtered through previously ignited asbestos before using. This will be called solution "A." And it will be observed that the solution had not been crystallized. After solution was complete, the three tests were filtered into platinum boats, and three combustions made. Two of these combustions were made in glass tubes, using exactly the same amount of combustion mixture as in case of the blanks above described, and following the

same manipulation, except that the boats with their carbon were buried in the combustion mixture in the tube. The third combustion was made in the apparatus, and by the method previously described under the head of Dudley's Apparatus and Method. The results obtained from these three combustions were as follows :

	Per cent.
Combustion mixture No. 1, after allowing for blank, gave, carbon . . . . .	1.102
Combustion mixture No. 2, after allowing for blank, gave, carbon . . . . .	1.109
Combustion with Dudley's apparatus and method . . . . .	1.106
Average . . . . .	1.106

These results were regarded as showing that Dudley's apparatus and method gave fairly reliable results so far as the combustion was concerned.

But these results were confirmed by two further tests, as follows : First—A direct combustion of crystallized and pulverized sugar in the same apparatus, and immediately following the last steel analysis above, gave,

Carbon . . . . .	42.02 per cent.
Theoretical carbon in sugar . . . . .	42.11 "

This was followed, secondly, by a blank combustion, everything being done exactly as in a regular combustion, except that nothing was put in the combustion tube. This blank showed a loss in the weight of the absorption apparatus of two-tenths of a milligramme.

The apparatus and method being regarded as satisfactory, attention was next given to the release of the carbon. Experiments were planned to demonstrate the effect of different states of dilution of the double chloride solution on the release of the carbon ; also, to determine whether large or small amounts of double chloride solution changed results, and also to determine whether varying amounts of chloride of ammonium relative to the chloride of copper present produced any change. Before this part of the work was fairly entered on, however, a shipment of crystallized double chloride was obtained from the market. Since it had already been noticed in the work done on apparatus and method

previously alluded to that discordant results were frequently obtained, it was at first suspected that the apparatus and method were at fault, but after the tests of the apparatus, above given, were made, suspicion fell on the double chloride, and accordingly a nearly saturated solution was made from the shipment above alluded to. This solution will be called solution "B." Four combustions of the experimental standard ingot were made, using 200 cc. of solution "B" rendered acid with 10 cc. of HCl. These gave results as follows :

No. 1, Carbon . . . . .	L.070
" 2, " . . . . .	1.067
" 3, " . . . . .	1.060
" 4, " . . . . .	1.065
Average . . . . .	1.065

These results, it will be observed, are a trifle over .04 per cent. lower than were obtained with the same steel, with the same apparatus and method, but using the uncrystallized double chloride solution "A." The problem at once arose how to reconcile these discrepancies. Obviously, if the apparatus and method could be trusted, either the solution "A" contributed something to the absorption apparatus, which was weighed and counted as carbon, or solution "B" dissolved and carried off some of the carbon in the steel—or possibly both. Who could tell where the truth lay?

The first attempt to unravel the mystery consisted in taking 450 cc. of solution "A" with 25 cc. of HCl, and adding to it 1 gm. of steel. After the reaction was complete and the solution had been thoroughly mixed, it was filtered through asbestos. The result of this treatment was that this 450 cc. of solution "A" had now in it some sub-chloride of copper, some chloride of iron, and also carbon liberated from steel had been floating around in it, affording an opportunity for any material which might be separated from the solutions by the reaction to attach itself and be filtered out. The reasoning was as follows: If double chloride solution "A" contains any carbonaceous material in solution which separates when the solution is treated with steel, thus causing high results, a part, at least, of this material will separate when the 450 cc. are treated with one gm. of steel, and be removed by the subsequent filtration, and consequently combustions made,



using this treated double chloride solution "A," will show lower results. Two combustions were accordingly made of the experimental standard ingot, everything being exactly as in the previous combustions, except the use of the treated double chloride solution "A." These combustions gave :

No. 1, Carbon . . . . .	1.076 per cent.
" 2, " . . . . .	1.070 "
<hr/>	
Average . . . . .	1.073 per cent.

Here was a reduction of a little over .03 per cent. from the figures obtained using solution "A" untreated with steel, and the figures seem to indicate quite clearly that uncrystallized double chloride solution "A" contained something in solution that separated during the reaction with the steel, and gave erroneous and too high results.

In confirmation of this view, the following experiments were made : 200 cc., the usual amount for a combustion, of solution "A" with 10 cc. of acid were treated with 5 gms. of experimental standard ingot, instead of 3 ; the assumption being, if there is a certain amount of carbonaceous matter in solution "A" which comes out during the reaction with the steel, lower results will be obtained if this error is divided over a larger amount of steel. Two combustions were made on this plan, which gave results as follows:

No. 1 gave, Carbon . . . . .	1.049 per cent.
" 2 " " . . . . .	1.082 "
<hr/>	
Average . . . . .	1.065 per cent.

It is possible the first of these duplicates is a little low, as this carbon sponge from the larger amount of steel was a little difficult to manage in the boat; but as both the results are lower than those previously obtained from solution "A," it is evident they point in the direction that there is something in solution "A" that should not be there.

One more experiment was made on solution "A," as follows: 1000 cc. of this solution was treated with 50 cc. of HCl, and allowed to stand for some time. This solution was then filtered on the boat, and although nothing was visible to the eye, a combustion was made. The absorption apparatus showed an increase in

weight of  $3\frac{1}{2}$  milligrammes. This corresponds to a trifle over .006 per cent. of carbon in the steel which had been used in all the previous tests. This apparently indicates that although solution "A" probably contains something which it should not, that something only separates very slightly when the solution is treated with acid.

Thus far the evidence seems to point quite strongly in the direction that uncrystallized double chloride solution contains some carbonaceous matter which separates during the reaction with the steel. But who knows that crystallized double chloride does not also contain carbonaceous matter? And still further, who knows that either crystallized or uncrystallized double chloride does or does not dissolve some of the carbon of the steel during the reaction, and thus produce a loss?

Upon the first of these questions the following experiments were made: 450 cc. of solution "B," which, it will be remembered, was made from crystallized double chloride obtained from the market, were treated with one gm. of steel and acid, as previously described for solution "A," and two combustions made. These two combustions gave:

No. 1, Carbon . . . . .	1.060 per cent.
" 2, " . . . . .	1.061 "
<hr/>	
Average . . . . .	1.060 per cent.

These results are, it will be observed, only about .005 per cent. lower than were obtained with the same solution untreated with steel, and seem to indicate that crystallization removes at least the largest part of the carbonaceous material, such as was characteristic of solution "A." But the mother liquor, from which the crystals forming solution "B" were obtained, may not have contained any large amounts of carbonaceous matter, and so the evidence seems most conclusive.

In continuation of this same study, four more combustions were made, two of them using solution "B," but no acid, and the other two likewise using solution "B" and no acid, but treating the solutions with steel, as previously described. These combustions showed as follows:

	Untreated.	Treated.
No. 1, Carbon . . . . .	1.036 per cent.	1.030 per cent.
" 2, " . . . . .	1.035 "	1.024 "
Average . . . . .	1.035 per cent.	1.027 per cent.

These results show about .008 per cent. lower for the treated double chloride than for the untreated, but the number of analyses and the number of samples of crystallized double chloride experimented on, seem hardly sufficient to set at rest the questions as to whether crystallization completely removes the probable difficulty due to carbonaceous matter in the mother liquor.

Thinking that possibly carbonaceous matter might be introduced into the double chloride solution "A" by the commercial chloride of ammonium used in making it, four combustions were made, using some of the same shipment of chloride of copper alone which had been used in making solution "A." All four of the solutions had acid present, and two of them were made with the solution previously treated with one gm. of steel and filtered as already described; the other two not treated. The same steel was used as in all the previous cases; these combustions gave the following results:

	Untreated.	Treated.
No. 1, Carbon . . . . .	1.072 per cent.	1.040 per cent.
" 2, " . . . . .	1.056 "	1.050 "
Average . . . . .	1.064 per cent.	1.045 per cent.

These figures, as will be observed, seem to indicate that part of the difficulty, at least, is due to the chloride of ammonium, since the chloride of copper alone gives nearly .04 per cent. lower results than solution "A." They also seem to indicate that previous treatment with steel throws out something from even the chloride of copper alone. Too much importance should not, however, be attached to these results, as the reaction between the chloride of copper and the steel was very slow; and as acid was present, and it was impossible to keep the solution agitated continuously, it is probable a slight loss of carbon may have occurred. The variation in the duplicates may possibly be accounted for in this way.

Up to this point the evidence obtained seems to indicate: 1st, that uncrystallized double chloride made from commercial materials probably contains carbonaceous matter in solution; 2d, that

this may come partly from the chloride of copper, and partly from the chloride of ammonium ; and 3d, that crystallization is probably advantageous in diminishing, if not completely removing, this difficulty. But some points are not quite certain, and accordingly the following experiments were undertaken to throw as much light as possible on the subject.

Commercial chloride of copper and commercial chloride of ammonium were obtained from the market. These were dissolved in hot water and mixed in the proportions to give a salt containing one molecule each of the two chlorides. On cooling the hot solution to a low temperature a large crop of crystals of the double salt was obtained. The mother liquor was drained off from these crystals and set aside. Also a portion of the crystals obtained were rinsed with pure water and set aside. The remainder of the crop of crystals was again dissolved in hot water, evaporated a little and cooled, giving a second crop of crystals, from which the second mother liquor was drained off ; they were then rinsed with pure water. The first and second crop of crystals were then each dissolved in water, forming nearly saturated solutions at ordinary temperatures. This gave three solutions to work with, viz.: (1) The mother liquor from the first crop of crystals, (2) a solution of the first crop of crystals, and (3) a solution of the second crop of crystals. In other words, solutions of uncrystallized, once crystallized, and twice crystallized double chloride. The mother liquor solution was treated with ammonia sufficient to give a slight precipitation, and then filtered through asbestos. It was then divided into two parts, and one part treated with HCl to the amount of 5 per cent. The part treated with ammonia alone we will call basic mother liquor, and the other acid mother liquor. Three combustions each were made with these two solutions, using the same steel and everything else as previously described. The results obtained were as follows :

	Basic Mother Liquor.	Acid Mother Liquor.
	Per cent.	Per cent.
No. 1, Carbon . . . . .	1.086	1.145
" 2, " . . . . .	1.081	1.130
" 3, " . . . . .	1.067	1.150
Averages . . . . .	1.078	1.141

Two results are quite noticeable in these figures : 1st. The acid mother liquor gives higher results than any previous determination ; and, 2d. The differences between the basic and acid solutions is greater than in any previous case.

The second solution, viz., that from the first crop of crystals, was divided into two unequal parts. The smaller of these was treated with ammonia and filtered as previously described, forming what we will call basic first crystals. The other part was filtered through asbestos and divided into two parts, one of which was treated with acid, as above described, and will be called acid first crystals. The other part was left without further treatment, and will be called neutral first crystals.

Three combustions each were made with these three solutions, showing as follows :

	Basic First Crystals.	Neutral First Crystals.	Acid. First Crystals.
	Per cent.	Per cent.	Per cent.
No. 1, Carbon . . . . .	1.026	1.029	1.070
" 2, " . . . . .	1.017	1.034	1.081
" 3, " . . . . .	1.031	1.029	1.082
Average . . . . .	1.027	1.031	1.077

The marked diminution in the amount of carbon between the mother liquor and the first crop of crystals is very noticeable. In the basic results the difference is .051 per cent., and in the acid results the difference is .065 per cent. It will also be observed that there is a slight difference between the basic and neutral.

With the second crop of crystals only basic and acid combustions were made, the solutions being obtained as previously described. The results obtained were as follows :

	Basic Second Crystals.	Acid Second Crystals.
	Per cent.	Per cent.
No. 1, Carbon . . . . .	1.016	1.049
" 2, " . . . . .	1.028	1.056
" 3, " . . . . .	1.023	1.052
Average . . . . .	1.023	1.052

These results, taken in connection with what precedes, are, to our minds, exceedingly interesting. The marked diminution in the amount of carbon obtained with the second crystals over the

mother liquor, especially in the acid solutions, cannot fail to be noticed, and this would seem to indicate that double chloride made from commercial materials without crystallization contains carbonaceous matter. This point would seem to be settled if it were not for the doubt whether the double chloride does not dissolve some of the separated carbon. Upon this point no positive data have yet been obtained. Two points further seem worthy of note. 1st. The basic first and second crop of crystals give practically the same results, while the acids do not. And 2d. The farther away from the mother liquid the nearer the results from the basic and acid treatment come together. To our minds, these facts, together with what precedes, seem to indicate that possibly the commercial material contains dissolved cellulose, and that crystallization diminishes the amount of this, so that with the material used in the above experiments, once crystallizing diminished the amount of cellulose, so that the basic liquid retained in solution what was left, since alkaline oxide of copper is a well-known solvent of cellulose, while the acid solution, even of the twice crystallized salt, still gives up a little cellulose to the carbon sponge.

In the special ground covered by Dudley in a study of the release of the carbon, the results of which are given quite at length above, the services of Dudley's principal assistant, Mr. F. N. Pease, have been found of the greatest value. He made all the combustions, and his suggestions have been most pertinent and useful.

A few attempts have been made to estimate the carbon in the Exp. Standards by methods not employing double chlorides, but with not much success.

Langley had proposed dissolving the steel in a hot solution of copper sulphate made as nearly neutral as possible, then filtering and burning the mixed copper and carbon sponge in oxygen. (American Association Advancement of Science, vol. 24, 1875.)

This method occasionally gives too low results, because of the impossibility of being sure that the last particles of steel are dissolved. Dudley made the following trials on the Ingot Standard.

$\text{CuSO}_4$  was ignited to remove possible organic matter, then dis-

solved and filtered. The solution was made as neutral as possible, and allowed to stand on the steel several days. Result :

Carbon	. . . . .	1.011	per cent.
"	. . . . .	.972	"

Then to 300 cc. of the sulphate solution was added 15 cc. HCl. The attack of the steel was rapid, but some gas was evolved. Result :

Carbon	. . . . .	1.002	per cent.
"	. . . . .	1.036	"
"	. . . . .	1.040	"

He then tried attacking the steel by solid silver chloride under water, and burning the silver and carbon sponge. Result on Hammered Standard :

Carbon	. . . . .	.796	per cent.
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Langley made two determinations by putting the steel directly into the chromic-sulphuric acid mixture, without previous treatment by chlorides. Result on Hammered Standard :

Carbon	. . . . .	.788	per cent.
"	. . . . .	.790	"

In this case more gas was evolved than what corresponded to the  $\text{CO}_2$ . It was found that methane would pass through the boiling chromic mixture without sensible oxidation ; therefore, some of the carbon of the steel may have escaped in union with hydrogen.

#### SUMMARY.

The conclusions here presented are not those of the committee in their official capacity. They are the views provisionally held by the members whose work is given above.

First. The combustion of carbon in a porcelain tube in a stream of purified oxygen, when the precautions indicated are used, gives sensibly accurate results.

Second. If the carbon contains chlorine, it is desirable to use a coil of metallic silver in the combustion tube, and it is apparently also *essential* to use some solution of silver, preferably the sulphate, in the purifying train.

Third. The chromic acid method is capable of burning all the carbon used. If this carbon also contains chlorine, it is *essential* to use some deoxidant in the purifying train, preferably pyrogalllic acid with oxalate of potash ; also a liquid silver absorbent must

follow the deoxidizing tube. Under these conditions, this method gives sensibly accurate results.

Fourth. The use of a small quantity of HCl in a solution of the double chloride of copper and ammonium invariably gives higher results than when a neutral solution is employed.

Fifth. There is no evidence that the substitution of KCl for  $\text{NH}_4\text{Cl}$  in the double chloride is of any advantage.

Sixth. The most important discovery made by the committee in this work pertains to the variable action of the double chloride solutions. This apparently throws doubts on the reliability of all carbon determinations previously made by this reagent, since they show variations on the same steel lying between 1.016 and 1.150.

When the degree of acidity is kept constant, the apparent quantity of carbon found is affected by the mode of preparation of the double chloride, by its age, and by the number of times it has been crystallized.

Seventh. A carbon sponge derived from a double chloride solution does not appear to lose any carbon by drying at a temperature under  $100^\circ \text{C}$ ., but loses if the heat is higher. The problems now before the committee, as suggested by the above results, are : The determination of carbon in steel by some direct process not involving the use of double chloride ; the direct combustion of finely divided metal in oxygen or chromic acid is one of these, or by fusion in a mixture of bisulphate and bichromate of potash.

The determination if possible, whether a neutral or alkaline double chloride liquid, may not dissolve a portion of the carbonaceous residuum, and thus lead to results which are too low.

The determination, whether the addition of acid simply, prevents this tendency, or whether the use of acid may not favor the separation of pre-existing organic matter in the liquid, and its retention by the carbon sponge, thus leading to results which are too high.

The investigation of the cause of the influence of repeated crystallizations of the double chloride on the apparent quantity of carbon.

Finally, it is to be presumed that many, if not all of the above points, have attracted the attention of other analysts : and the committee will be glad to learn of the results and experience of others along these lines.



## A NEW METHOD FOR STANDARDIZING THE SOLUTIONS USED IN ALKALIMETRY AND ACIDIMETRY.

BY EDWARD HART AND STUART CROASDALE.

Several substances have been proposed and used as materials for determining the strength of the standard acid and alkaline solutions used in volumetric saturation analysis, among them sodium carbonate, oxalic acid, and acid potassium oxalate. All of these substances have disadvantages, especially where a great degree of exactness is necessary. Sodium carbonate, which, following Mohr's recommendation, has been most commonly used, is, as found in commerce, seldom quite pure. This was long ago pointed out by Stas. It has the further disadvantage that it must be ignited gently and weighed quickly after cooling, as it takes up moisture from the air quite rapidly. Another disadvantage is that the solution when titrated against an acid must be boiled to drive off carbon dioxide before the titration can be finished. All these things require time. As the volumetric method is especially designed to save time, these disadvantages are serious ones. The difficulty of getting oxalic acid of proper purity, and of protecting it from loss of water of crystallization, is so well known that it need not be considered further. The same thing holds true, to some extent at least, of acid potassium oxalate. Any crystalline salt is sure to be subjected to more or less suspicion from the impossibility of so preparing it that no water shall be included between the crystals, or that no hygroscopic moisture shall be left adhering to the crystals, or that some of the water of crystallization may have been driven off by too sharp drying. We have therefore devised a method which avoids all these sources of error and which for exactness leaves nothing to be desired, and is extremely convenient and easy of execution.

The electrolytic assay of copper has long been known to yield very accurate results when properly carried out, but has recently been subjected to some criticism by English chemists. In order to test the matter, a very large number of analyses have been made in this laboratory, which will soon be ready for publication. The result of this investigation has convinced us that with proper precautions the assay is one of the most accurate known. In or-

dinary cases, where from .1 to .2 gms. copper are to be thrown down, the differences in duplicate assays never exceed .0002 gm., and generally do not exceed .0001 gm.

When normal copper sulphate is subjected to electrolysis, for every 63 parts copper thrown down 98 parts sulphuric acid are set free, and, if we use pure copper sulphate, at the end of the operation we shall have all the copper adhering to the dish and a corresponding amount of pure sulphuric acid in solution. The copper is weighed as accurately as possible, and a simple calculation shows at once the amount of sulphuric acid in solution, which has thus virtually been weighed, and may be at once used for standardizing caustic soda or other alkaline solution with which in turn standard acids can be compared.

A solution of pure copper sulphate when as dilute as this is not a very good conductor, and it is best therefore to add a small quantity of neutral potassium or sodium sulphate solution before the electrolysis is started.

The following examples illustrate the method, and show what accuracy can be attained when working in the ordinary rapid way.

Two roughly weighed samples of commercial C. P. copper sulphate were electrolyzed, and gave :

$$\begin{array}{r} \text{Cu} = \text{H}_2\text{SO}_4 \\ (1) \ .1015 = .15789 \\ (2) \ .1079 = .16784 \\ \hline .2094 = .32573 \end{array}$$

The acid resulting was then used to standardize a caustic soda solution, which it was intended to dilute to decinormal strength. Phenol-phtalein was used as indicator.

$$\begin{array}{r} (1) \text{ required } 3.4 \text{ cc. of the caustic soda solution} \\ (2) \text{ " } \quad \quad \quad 3.6 \text{ " " " " " " } \\ \hline 7.0 \\ \\ \frac{4.900}{.32573} = 15.043; 15.043 \times 7. = 105.30 \end{array}$$

In the above calculation, the atomic weight used for copper was 63, and the molecular weight of sulphuric acid was taken as 98.

The decinormal solution was then made up, using 105.3 cc. per liter of the strong solution.

A more careful calculation, using the atomic weight 63.18 for copper and the molecular weight 97.82 for sulphuric acid, showed that the amount used was too small.

$$\begin{aligned}(1) .1015 \text{ Cu} &= .15715 \text{ H}_2\text{SO}_4 = 3.4 \text{ cc.} \\(2) .1079 \text{ " } &= .16706 \text{ " } = 3.6 \text{ "}\end{aligned}$$

$$\frac{4.891}{.15715} \times 3.4 = 105.808$$

$$\frac{4.891}{.16706} \times 3.6 = 105.39$$

$$2) 211.198$$

$$105.599$$

The decinormal solution will therefore turn out to be too weak. This decinormal solution was then titrated against sulphuric acid obtained in the same way, as follows :

$$\begin{aligned}(3) .1062 \text{ Cu} &= .16442 \text{ H}_2\text{SO}_4 = 34.15 \text{ cc. decinormal soda.} \\(4) .1065 \text{ " } &= .16495 \text{ " } = 34.35 \text{ " " " " } \\(5) .1049 \text{ " } &= .16241 \text{ " } = 33.9 \text{ " " " " } \\(6) .1060 \text{ " } &= .16412 \text{ " } = 34.2 \text{ " " " " }\end{aligned}$$

$$1 \text{ cc. will therefore equal } \left\{ \begin{array}{l} (3) .004814 \text{ H}_2\text{SO}_4 \\ (4) .004802 \text{ " } \\ (5) .004791 \text{ " } \\ (6) .004799 \text{ " } \end{array} \right\} \text{Mean, .0048015}$$

The behavior of the solution at the point when neutralization was nearly reached led us to suspect that the copper sulphate was not quite pure, for the solution became light pink, and this color slowly faded. If another drop was added, the same process was repeated, and this continued until 4 or 5 drops had been added, when the solution took a permanent pink tint.

We therefore prepared a new lot of copper sulphate by heating electrolytic copper with pure concentrated sulphuric acid and recrystallizing the product eight times. Three determinations with this product gave the following results :

$$\begin{aligned}(7) .1021 \text{ Cu} &= .1581 \text{ H}_2\text{SO}_4 = 32.8 \text{ decinormal soda.} \\(8) .1041 \text{ " } &= .1612 \text{ " } = 33.5 \text{ " " } \\(9) .1050 \text{ " } &= .1626 \text{ " } = 34.1 \text{ " " }\end{aligned}$$

$$1 \text{ cc. will therefore equal } \left\{ \begin{array}{l} (7) .0048194 \text{ H}_2\text{SO}_4 \\ (8) .0048112 \text{ " } \\ (9) .0047674 \text{ " } \end{array} \right\} \text{Mean} = .0047993$$

Mean of 7 determinations, .0048006.

In (7), (8) and (9) the same fading of the pink tint occurred as in the first lot. This was traced to a little carbonate in the caustic soda, for when the solution which had lost color was boiled, the pink tint reappeared. We have no doubt that with a burette with very fine point, still closer results can be obtained; but for any ordinary work, the above are sufficiently accurate.

#### A MODIFIED METHOD OF EXECUTING THE POTASSIUM FERROCYANIDE TEST IN GLUCOSE DETERMINATIONS.

By B. B. ROSE.

In estimating glucose by Fehling's method, as ordinarily followed by sugar chemists, the end point of the reaction is determined by testing a small portion of the filtered solution for copper by means of potassium ferrocyanide in the presence of acetic acid. The filtration is generally effected by means of glass tubes tipped with a muslin filter and asbestos pulp, the tube being rinsed and fresh pulp applied after each test.

A somewhat simpler method of removing a portion of the solution for examination has been lately introduced in this laboratory, and has been found quite easy of execution.

A small filter, whose diameter need not exceed two inches, is folded as for ordinary filtrations, and is immersed, point down, in the hot supernatant liquid, the apex of the filter being just beneath the surface of the solution.

A portion of the liquid at once filters through, and is removed from the interior of the filter by means of a small dropping pipette, consisting of a small glass tube with point finely drawn out, and provided with a rubber bulb at the upper extremity.

The liquid is readily taken up and expelled from the pipette by first compressing and then relaxing pressure upon the bulb.

A fresh filter is used for each filtration, and the pipette is rinsed after each portion of the solution is tested. It is found that the

quantity of solution absorbed by the filter is inconsiderable, and affects the results inappreciably when no tests are made until the precipitation of the copper is nearly complete.

In addition to its simplicity, the economy of time and labor afforded by its use, renders this method quite advantageous where many determinations of this character are to be made.

CHEMICAL LABORATORY,  
STATE UNIVERSITY AND A. & M. COLLEGE,  
BATON ROUGE, LA.

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### THE FILTRATION OF NATURAL WATERS.\*

BY THOMAS M. DROWN, MEMBER BOSTON SOCIETY CIVIL ENGINEERS.

In the study of the subject of filtration of water for drinking purposes, we shall arrive at no clear and valuable ideas unless we distinguish sharply between mechanical filtration, which deals only with the interception and retention in the filter of the solid particles suspended in the water, and filtration combined with the oxidation of organic matter, — that in solution, as well as that in suspension in the water. This latter process—the purification of the water by the oxidation of its organic contents—can be accomplished only by *intermittent* filtration, the former—the mere removal of the solid particles in the water—may be accomplished by *continuous* filtration, as practiced in many large cities in Europe.

When we speak of the purification of water by filtration, we mean in general a way, that a water is thereby rendered fit to drink which was unfit or unattractive before it was filtered. The change effected by filtration may be simply the removal of vegetable or earthy matters, whereby the water is made more palatable and more attractive in appearance, or it may be more radical, in converting water which was positively harmful into a good drinking water. Widely different in action as are the two systems of filtration, the intermittent and the continuous, yet it is possible by both systems to improve the quality of a bad water.

In the system of continuous filtration, in which there is little or no change made in the dissolved organic matter, it might at first thought seem as if there could be only imperfect purification ; but

\*From a paper read January 15, 1890. Reprinted in part from the Journal of the Association of Engineering Societies.

it must be borne in mind that it is possible in this system to remove in great part even those very minute organisms, the bacteria.

The germ theory of disease furnishes us with the simplest explanation of the way in which water does harm, and if we can, by simple mechanical filtration, remove the harmful germs from the water, we have effected a true and efficient purification of that water, whatever may be its chemical composition. Let us push this idea a little further. If we take as the basis of our theory of harmfulness of water that disease is caused by it only when micro-organisms are present in it, then, if we could by the continuous filtration of sewage remove absolutely all the germs which it contained leaving unchanged its other characters—appearance, taste, odor, etc.—this sewage would be perfectly safe to drink. To put the matter in another form, a sterilized water or sewage has no possibilities of producing disease except so far as it may contain saline or other substances which may produce derangements of the system in the same way as would a drug—a dose of salts or of senna. It is foreign to my present purpose to consider whether our knowledge at present justifies this position, but it is important to bear it in mind in judging of the efficiency of filtration.

When water is said to be well, or moderately well, or completely purified by filtration, we cannot know what is meant unless we know what is the standard of purity implied. Is it simply the removal of color, odor and suspended matter; is it chemical purity, meaning thereby the absence of unoxidized organic matter, or is it bacterial purity, or freedom from germs? Again, what shall we say of water of high chemical purity, with high bacterial contents; or what of a water with few or no bacteria which contains considerable organic matter capable of undergoing change?

Intermittent filtration is capable of giving water free from organic matter and free from germs; continuous filtration, if conducted very slowly, is capable of giving water free from bacteria, without odor and color, but which may contain much dissolved organic matter. Intermittent filtration effects the oxidation of the organic matter in solution as well as that in suspension; continuous filtration has little or no effect on the organic matter in solution.

After laying such stress on the removal from water of bacteria,

it sounds like a paradox to say that purification both by intermittent and continuous filtration depends on the presence in the filter of bacteria in enormous numbers, and that without them the purification would in both cases be impossible.

The idea is not a new one that the bacteria of decomposition are benign and useful organisms which break up organic matter, rearrange its atoms and convert it into mineral matter so that it may again serve as food for plants. If we keep away the bacteria from a mass of dead organic matter it undergoes no change whatever. All processes of decay of organic matter are absolutely dependent on the presence of these micro-organisms, which, so far as we know, have no other than a beneficent role to play in nature. I say this is now a matter of common knowledge and one is therefore not unprepared to hear, that in the purification of water by intermittent filtration the ground or sand upon which the water is poured is full of bacteria, in fact, that it is the design of the process to cultivate them and have as many of the micro-organisms in a cubic inch of ground as possible.

If one pours over a column of clean, bright sand, free from bacteria, impure water, as sewage, it will flow out about as bad as it entered the sand. But if it is poured over a column of sand in which septic bacteria have been cultivated, so that the sand may be said to be fairly reeking with bacteria by the million, the water may flow out as pure (organically) as spring water. But even in continuous filtration, where there is little or no oxidation going on the bacteria are, according to Piefke, (the engineer of the Berlin water works,) the efficient agents in removing the suspended matters, including the micro-organisms in the water. To this subject we will return later; let us first briefly study the nature of oxidizing or intermittent filtration on the typical polluted water, namely sewage.

Sewage is a substance which contains all of its nitrogen in the unoxidized form. Its principal ingredient is free ammonia; it also contains considerable, (but a much less amount, usually,) organic nitrogen, or albuminoid ammonia, but of nitrous or nitric acid it contains none. When sewage is exposed to the air in mass, oxidation goes on very slowly, because it can only get air from its surface; when it flows out into streams, the oxygen dis-

solved in the water of the streams quickly oxidizes the ammonia, and we find in the water a short distance below the entrance of the sewage, nitrites and nitrates abundantly. When the sewage is exposed to the air in very thin layers, as when a porous material like sand is moistened with it, oxidation goes on with great rapidity. It was until recently considered that this oxidation was a direct chemical combination of the elements of the organic matter with the oxygen of the air, or the oxygen dissolved in the water, but we now know that nitrogen is not oxidized by the direct contact of decomposing nitrogenous matters with air, unless bacteria are present, and the inference seems a fair one that the greater the number of bacteria the more rapid the process of oxidation. Sewage itself usually contains hundreds of thousands of bacteria to the cubic centimeter which are dormant until air gets access to it. If sewage is preserved out of contact of air, the bacteria of decomposition will in time all die.

The experiments of the Massachusetts State Board of Health on the purification of sewage by intermittent filtration which have been carried on at Lawrence for the past two years, under the direction of Mr. Hiram F. Mills, the engineer member of the Board, have added largely to our knowledge of the conditions governing the purification of nitrogenous organic matter. Here are large tanks, one two-hundredth of an acre in surface, filled with different materials—coarse sand, fine sand, river silt, muck, garden soil, clay, etc., to the depth of five feet, on which is poured, from day to day, sewage in known amount and of known composition. The effluent water from this sewage filtration is collected, measured and analysed and the precise amount of purification determined. The result of two years' work at this station will shortly be published in the Report of the Board now in press. I will at present give one or two of the facts that have been there developed. The purification of the sewage means the complete oxidation of all its organic ingredients both in solution and in suspension, the carbon to carbonic acid, the hydrogen to water, and the nitrogen to nitric acid. The filtering materials best adapted to the purpose are those which are fine enough to retain considerable sewage in their pores and also plenty of air at the same time.

The body of porous material is, when in good working order, a



very delicate machine. It must be coaxed up to its highest efficiency by gradually increasing the amount of sewage. This means, in all probability, that we must develop in the pores of the sand an immense number of bacteria to be constantly on hand in the different layers to attend to the sewage as it reaches them. During the first winter there was no nitrification in these tanks, and consequently no perfect purification, but on the advent of spring, when the temperature of the effluent water reached 39° F. nitrification began and has continued ever since, the cold weather of the second winter failing to stop it.

The tank which has given the best results, that is, a good purification of the largest quantity of sewage for a long period is filled with coarse mortar sand, most of the grains of which average about 0.06 in diameter. This has given an effluent day after day organically as pure as many drinking waters, when receiving sewage at the rate of nearly 60,000 gallons per acre per day.

One would naturally ask why is not this the ideal system of purification of all surface waters, even those that are not polluted by drainage of any kind, but which contain much vegetable suspended matter, and have, in consequence, sometimes, a bad odor; or waters which are unattractive in appearance by reason of dissolved coloring matter?

One of the tanks of the Lawrence Experiment Station has filtered Merrimack water intermittently for more than two years at the rate of 300,000 gallons per acre per day. The filtering material consists of 3' 8" of coarse and fine sand and fine gravel; 10" of yellow sandy loam, and 6" of brown soil in the same position as found on the river bank. During the day the surface of the sand is generally covered with a few inches of water, but at night and on Sunday air gets access to the sand. The following figures give the composition of the filtered water during last December, compared with the Merrimack water applied:

	MERRIMACK RIVER WATER.	FILTERED WATER.
	Parts per 100,000.	Parts per 100,000.
Turbidity . . . . .	very slight	none
Sediment . . . . .	very slight	none
Color . . . . .	0.35	0.0
Odor . . . . .	faintly vegetable	none

Total solids . . . . .	4.2	3.5
Loss on ignition . . . . .	1.6	0.9
Free Ammonia . . . . .	.0015	.0005
Albuminoid Ammonia . . . . .	.0127	.0059
Chlorine . . . . .	.18	.18
Nitrogen as Nitrates . . . . .	.0124	.0191
Nitrogen as Nitrites . . . . .	none	none

The water is free from microscopic organisms, and the bacteria rarely exceed 10 or 20 per cubic centimeter, while the water applied has generally a few hundred. During the two years that this tank has been in operation the surface has not been cleaned or disturbed in any way. The slow rate of filtration (being only about one-half an inch an hour per square foot of surface) is due to the considerable amount of very fine material contained in the soil and loam.

But one must bear in mind, in connection with the rate of filtration, that the thoroughness of the purification, meaning thereby the oxidation of the organic matter, is much greater in intermittent than in continuous filtration.

This system of intermittent filtration for natural waters has never, I believe, been carried out on the large scale, although the possibility of its being practicable in some localities has been discussed. It is the system that nature suggests, for it is intermittent filtration which supplies the springs which furnish the ideally pure and perfect drinking water. In the report of the Massachusetts State Board of Health to the Springfield Water Board with regard to the purification of the water of its Ludlow reservoir, which contains an immense growth of blue-green algæ, Mr. Stearns, the chief engineer of the Board, suggested that surveys be made to discover, if possible, suitable ground, conveniently situated, on which to pour intermittently the water of the reservoir and to collect it again at lower levels in wells and springs. It is probable that continuous filtration would be inapplicable to water of this kind, for the jelly-like masses which are secreted by these algæ would probably close the pores of the filter in a very short time. With intermittent filtration the deposit of organic matters in the pores of the sand would dry out or become oxidized when the ground was more or less dry.

It has been to many a difficult matter to explain how filters

working continuously, and constantly covered with water, could intercept objects so much smaller than the spaces between the particles of sand. It was easy to imagine that some of the minute suspended particles might be caught between the particles of sand, but that practically all the suspended matter, even the minute bacteria, could be removed in a good-working filter, seemed to indicate that the efficient working of a filter depended on the fact that it became nearly clogged on the surface by the algæ and other matter which held back even the smallest objects. But if this were the case, it would save time to use a finer sand at the outset which experiment shows will not accomplish the purpose.

Piefke\* has given us the clearest conception of the action of sand filters in removing the suspended matters including bacteria from surface waters. The chemical effect is very slight, as might be supposed when one reflects that the duration of the passage of the water through the sand seldom, if ever, exceeds five and one-half hours, and, since the filter is kept constantly covered, there is no oxygen present but that dissolved in the water. But the mechanical effect in removing suspended matter—mineral and organic—is very great. The Spree water, which forms part of the supply of Berlin, contains as high as 100,000 bacteria per cubic centimeter at times, and the number in the filtered water rarely exceeds 100, that is, the reduction of bacteria may reach 99.9 per cent. The thickness of the sand layer is generally from 2' to 3' and this rests on a layer of coarser gravel, which is without any effect on the filtration. The size of the sand is seldom finer than one-fiftieth of an inch, which leaves channels between the grains that 500 micro-organisms could pass abreast. Smaller still are the particles of clay which give a milkiess to water, and yet when one of these sand filters is working well, both clay and bacteria are held back in the sand.

It takes a new filter about two weeks to get to its maximum efficiency, and if the sand be first carefully cleaned and sterilized

\*Mittheilungen über natürliche und künstliche Sandfiltration. pp. 75, Berlin, 1881.

Die Boden Filtration, p. 51, Berlin, 1883.

Die Principien der Reinwasser Gewinnung vermittelst Filtration. p. 50, Berlin, 1887.

Aphorismen über Wasserversorgung von higienisch—technischen Standpunkte aus bearbeitet—Zeitschrift für Hygiene. 1889, Vol. 7, p. 115.

With C. Frankel—Ueber die Wirksamkeit der Sandfiltration zur Befreiung des Trinkwassers von etwaigen Infectionskeimen ; Zeitschrift für Hygiene, 1890. I.

by heat, then it takes much longer, many weeks, before the filter works well.

On examining with the microscope, the surfaces of the particles of sand when the filter is in perfect working order, they are found to be coated with a greasy, slimy substance which is a mass of bacteria jelly. Piefke found in a kilogram of sand taken from the surface of a filter 5,600,000,000 bacteria; just below the surface 734,000,000, and at the depth of a foot 92,000,000. These numbers, he says, are far below the truth, because of the difficulty of cleaning the particles of sand thoroughly. It is to this coating of bacteria jelly that Piefke attributes the efficiency of these filters, and until the jelly forms in sufficient amount to completely envelope each particle of sand, the filters work imperfectly. This then is his explanation of the fact that minute micro-organisms and particles of clay of infinitely smaller size than the channels in the sand are stopped in their passage through it—they are simply caught in this slimy coating and cannot get further.

A filter of this kind is, like that used in intermittent filtration, a very delicate instrument, and it is very easy to disarrange it. Disturbance of the sand or suddenly increasing the pressure of the water may have, as a consequence, a rush of bacteria into the filtered water. Quite regular working is an essential condition of success. The rate of filtration is on an average only four inches vertically an hour, so that in the passage of the water through the sand, one-third of which is interstitial space, its rate is three times as great, or twelve inches an hour, and the sand layer, being two feet thick, the water is in contact with the sand only two hours. In very turbid waters or waters very high in bacteria, the filtration is often decreased to one-half this rate or even less, and in comparatively clear water, with low bacteria, the rate may be doubled. The working of the filters in Berlin is governed entirely by the number of the bacteria in the filtered water, this being the simplest way of judging of the efficiency of their working. One hundred bacteria per cubic centimeter in the filtered water is considered a good result on the Spree water, which contains always many thousands. To give practically sterile water would require a diminished rate say to one vertical inch an hour, which would be impracticable without enlarging the filtering plant.

The surface waters used to supply London from the Thames or the Lee are filtered by the method of continuous filtration, a surface of one hundred acres being required for the purpose. The thickness of sand differs with the different companies supplying the city with water, from two feet at the East London and Grand Junction Companies to four and a half feet at the Chelsea Company, and the rate of filtration per hour in imperial gallons per square foot of filtering surface is two and one-sixth with the Lambeth Co., to one and one-half gallons with the Southwark & Vauxhall Co. Two and one-half gallons, or five vertical inches an hour (which is seldom attained) is considered the maximum consistent with good clarification. Complete analyses are made of the water supplied to the metropolis by the different companies. Some of the determinations, as for instance color, and the amount of permanganate to oxidize the organic matter, are made daily, other chemical determinations are made weekly. The monthly determinations made by Dr. Percy F. Frankland, of the bacteria in the waters of the different companies have been suspended since December, 1888. The average reduction of the number of micro-organisms present in the waters of the Thames and Lee, was in 1887, 97.6 per cent. in the case of the Thames, and 93.9 in the case of the Lee. "If," says the report on the metropolitan supply for December, 1888, "these figures could be accepted as at all representing the degree of security given to consumers of the waters of those rivers by preliminary filtration it is evident that the views on this subject acquired by a consideration merely of the results of comparative chemical analysis of filtered and unfiltered waters would have to be considerably modified and the character of the water supply would be correspondingly raised in the public estimation. Further, if the results obtained from month to month could be relied on as an index to the effect of filtration in eliminating objectionable matters from the water, the bacteriological method would seem to afford a delicate and easily applied test of the working efficiency of the filter."

The average numbers of bacteria in the water of the Thames is generally less than in the Spree at Berlin; thus during the year ending December, 1887, the highest number in November was 81,000, and the lowest in June was 2,200, the average for the year being 21,492.

The only filtering plant in this country, that I know of, which at all compares with the plants in Europe is that at Poughkeepsie where the Hudson river water is converted into good clear water, though not absolutely free from color. Mr. Fowler, the Superintendent of the works, writes me with regard to the details of the filtration, "Our usual rate of filtration is about six inches per hour, vertically, and this we regard as the maximum of efficiency, although we can sometimes do good work, so far as clarifying is concerned, at double that rate, and at other times are unable to do good work at one-half that rate, although the latter condition is exceptional. Very much depends upon the condition of the water in the river. The depth of water on the sand varies from one to three or four feet, and the difference of level between the surface of the water on the beds and that in the intermediate basins is usually two to four or five feet."

The rapid filtration of water through coarse gravel is not unfrequently carried out at water works to remove the larger particles floating in the water. When a filter of this kind is cleaned, it is surprising to see the amount of fine dirt of all kinds that has been intercepted by the coarse material. Filters of this character do not pretend to purify the water in the sense of removing bacteria or in oxidizing the organic matter, but they are useful just to the extent to which they clarify the water and thereby improve its appearance.

The American system of filtering large quantities of water may be said to be the mechanical filters working under pressure. These filters are composed of four or five feet of moderately fine sand (some have also a mixture of coke) enclosed generally in boiler-iron cases. They work with tremendous rapidity sometimes over a hundred vertical feet an hour, but forty feet is said by some to be the highest rate consistent with good filtration. In this system alum is generally added to the water as a coagulent. Its effect in very small amount is quite remarkable—say a grain to a gallon or even less—in retaining the solid matters of the water in the sand of the filter. The alum is decomposed by the carbonates in the water and hydrate of alumina is precipitated. This is a gelatinous and slimy substance, and immediately surrounds the algæ, clay and anything else that may be suspended in the

water, and the sand retains this coagulated mass. Alumina has also the effect of taking the color out of water, so that clear, colorless water may be obtained by this process from swampy waters full of growing algæ, with almost incredible rapidity.

These filters are in very general use in paper mills and other industrial works where a clear colorless water is needed, and where a colored turbid river water is the only natural supply available. They have also been introduced into some cities of considerable size, as, for instance, Long Branch, Chattanooga and Atlanta, and they are said to give water that is satisfactory to those who use it. The objection to the system is the use of alum. If all the alum used were decomposed in the few seconds that it takes the water to pass through the filter, so that no undecomposed alum passed into the filtered water, there might be no objection to its use, but this is not always the case. The amount of alum used is ordinarily small and it is claimed that if it even all went into the filtered water it would not injure it for drinking. This may be so but the prejudice that exists against drinking water which has been treated with "chemicals" is so strong that it is not likely that any system using a coagulant in a soluble form will find general acceptance. Under some conditions when the water has high color with much suspended matter the alum has to be increased largely to give good results. I have known as high as seventeen grains to the gallon to be used with a very bad swampy water.

In this connection should be mentioned the spongy iron filter of Bischof which gives most excellent results both in taking out suspended matters from the water, including the bacteria, and also decreases the hardness of the water. This filter has been used on the small scale in houses, and also on the large scale in Antwerp to decolorize and otherwise purify the water of that city. The filter is composed of finely divided metallic iron made by reducing iron ore by means of carbon at a temperature below fusion. Its action was not understood for a long time, and the mystery that surrounded it was an additional recommendation for it. The rationale of its working seems to be this, namely, that the iron being in a very finely divided state is dissolved to a slight extent by the combined action of the oxygen and carbonic acid in the

water, and the ferrous carbonate thus produced is further oxidized, forming hydrate of iron, and then this acts as a coagulent just as the alumina hydrate does. The system was said to be too expensive on a large scale, and it has now been replaced at Antwerp by the Anderson process in which the dark water is made to pass through a long revolving iron cylinder in which there is a large quantity of fragments of cast iron. These fragments of iron in their friction one on the other are abraded, minute particles are broken off which are dissolved in the way above described. The water coming from the revolving cylinder is exposed to the air, the iron oxidizes and precipitates, combines with the coloring matter in the water, encloses the solid particles, and is then filtered out through sand. The process is said to work satisfactorily and give clear colorless water. There is no objection to this use of iron as a coagulent, provided that it is all oxidized and precipitated, and none is carried in solution into the filtered water ; but this takes time.

Both alum and iron salts have a tendency to sterilize water. Their action may be both direct by killing the bacteria, and indirect by removing them with the precipitated alumina or iron hydrate. If a drop of a solution of alum, or of iron chloride be added to a gallon of turbid water, it will become perfectly clear in the course of a few hours, the alumina, or iron hydrate, which is formed in the water, settling to the bottom and carrying all the suspended matters with them. It has been proposed to clarify Mississippi water by adding a very small quantity of an iron solution to the water in the settling basins.

I have laid some weight on the desirability of following nature's processes in the purification of impure waters. Neither the American system with its mighty rush of waters or the European system with its calm, steady and deliberate flow finds any analogy in nature. In the rapid-working mechanical filters a coagulent is used to grasp and hold the suspended matter ; in the continuously working filter beds the bacteria are put to a novel use in retaining the solid matter on the sticky surface of the sand.

Nature uses these methods also ; she removes color by means of clay in the soil and intercepts mechanically in the bacteria-laden soil all the solid matter in the water, but she goes further than



this and, giving the bacteria full play, breaks up the organic compounds and leaves no trace of their existence behind. To do this, time is needed, "The bacteria of nitrification," as Dr. Smart has well said, in referring to the systems of rapid filtration, "cannot be harnessed to the work of artificial filtration."

The rate at which nature works may be expressed in the amount of rain-fall. If we take the rain-fall at fifty inches and assume that even half of this sinks into the ground (a very high estimate) we have twenty-five inches yearly on a square foot of surface. The amount of water which goes through the Berlin filters, at a rate of four inches an hour, is more than 1,250 times this amount. If we wish to imitate the process by which nature makes its springs, we must pour the water from river or lake which we wish, to filter intermittingly on the surface of ground which is favorable for this purpose. The favorable conditions are these: The ground must be sufficiently porous to allow the ready flow of water through it, and it must have such relations to the strata below as will enable us to collect the water at some lower level. It would not profit us much to pour the water on to a gravel bed if we could not find it again after it had been filtered. If the natural conditions for this purpose are not favorable, drains would have to be put in at suitable depths to collect the filtered water. Water purified in this way would in no wise differ from natural spring water, provided that the amount of water applied did not exceed the capacity of the filtering area.

The question of the maintenance of the purity of the water supplies of large cities, which are dependent upon surface waters, is daily becoming more urgent in this country as the population becomes more dense on the collecting areas, and the protection of streams against pollution becomes more and more difficult. The radical remedy in such cases is to take water from another and, usually, more distant region, which, it is probable, will never become thickly settled. But in filtration, both intermittent and continuous, when intelligently conducted, we have a substitute which can give as clear, colorless, and, we have good reason also to suppose, safe drinking water.

## APPARATUS FOR RAPID AND PROLONGED WASHING OF PRECIPITATES.

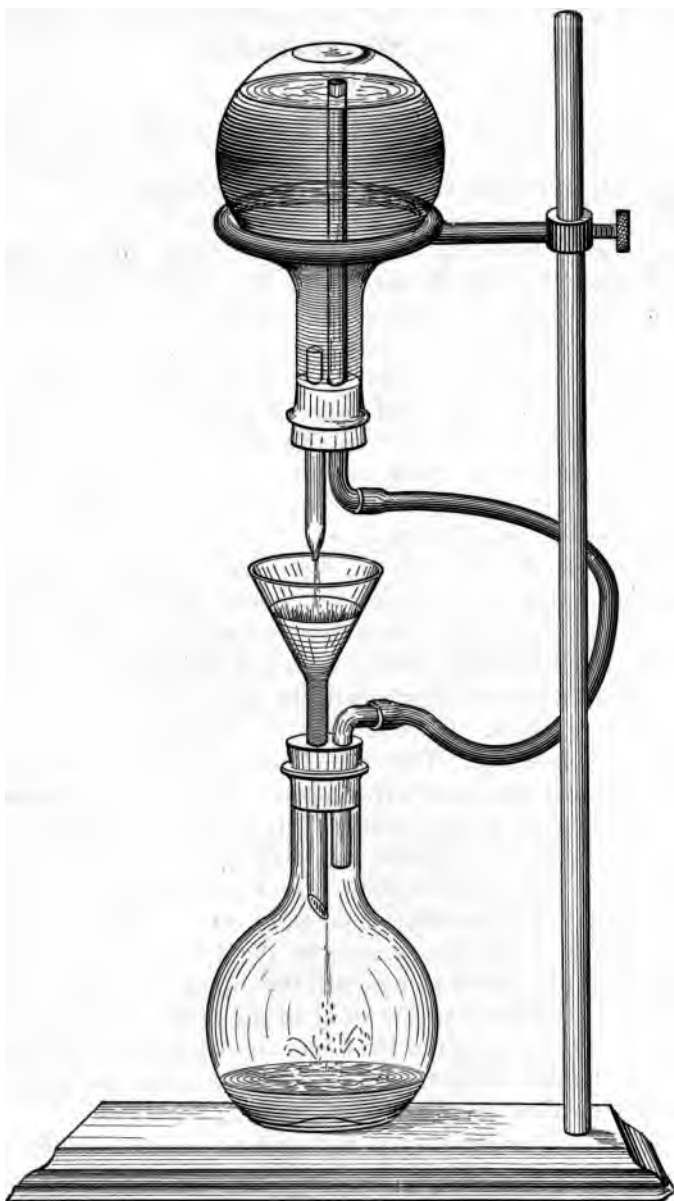
By R. W. Wood, Jr.

While trying to devise some form of apparatus that would supply a stream of pure water to a filter funnel at the same rate that it ran out, I hit upon the following simple device :

The diagram speaks for itself, a description being hardly necessary. Two good-sized flasks are fitted with rubber stoppers, which must be absolutely air-tight. Through the stopper of the bottom flask runs the tube of the funnel, and beside it another short piece, bent at a right-angle, is inserted. This latter piece connects, by means of a rubber hose, with a tube perforating the cork of the other flask and running to the top. The delivery tube, drawn out to a medium fine point, is fitted beside this, and the apparatus set up on a retort stand so that the orifice is about level with the mouth of the funnel. It is well to put a spring clip on the rubber hose.

If it is desirable to save the filtrate, the filtration had best be performed in the usual manner before inserting the cork into the lower flask. After the filtrate has run through, insert the cork holding the funnel, etc., into the neck of the flask : see that the filter paper is pressed tightly into the funnel so that no air may be drawn through. Open the spring clip on the hose and the flow will commence. The funnel will fill perhaps one-quarter full, and then the level will remain constant. If it is not full enough, pour in a little water. No change of level will occur after the equilibrium is once established, for no more water can flow out of the reservoir than runs through the filter into the lower flask. The downward pressure of the fluid in the upper flask creates a partial vacuum in the lower one, making the operation rapid, but in no case will the supply exceed the demand. If there is a tendency of the fluid to rise in the funnel, either air is being drawn through or the joints are not perfect. By looking through the side of the funnel, near the bottom of the paper cone, it is easy to see if any bubbles are running through.

This piece of apparatus will be found especially useful for washing sulphides with  $H_2S$  (in solution) when it is necessary to keep the precipitate out of contact with the air.



# THE DETERMINATION OF THEINE IN TEA BY THE KJELDAHL NITROGEN METHOD.\*

BY HARRY SNYDER.

A number of methods have been proposed for the quantitative determination of theine in tea, but most of them are long and tedious processes, and but little progress can be made by an analyst when a large number of teas are to be examined.

The introduction of the Kjeldahl nitrogen method, and its general application to foods and fodders, led to its use by myself for the determination of the total nitrogen in tea. The nitrogen in tea comes from two sources: the alkaloid theine,  $C_8H_{10}N_4O_2 \cdot H_2O$ , and the protein compounds. The protein compounds yield all of their nitrogen, but the question still remains, does the theine give up all of its nitrogen to form ammonia in this process of ammonification.

Kjeldahl,† with his original method (which has since been much improved), obtained 28.6 per cent. nitrogen, against 28.86 per cent. theory; Dafert,‡ after a careful study of the Kjeldahl method, found that the nitrogen can be accurately determined in the alkaloids. R. Austin§ and L. L. Hottel|| report similar results.

As a final test, a sample of theine was obtained, and the nitrogen determined in the ordinary way, and it yielded:

28.64	per cent. N
28.71	" "
28.74	" "

Theory, 28.86 per cent. N.      Average, 28.69      "      "

The substance contains so much nitrogen that only about 50 mgs. could be taken, without using too large a quantity of standard acid in the final titration. In order to obviate this difficulty the determinations were repeated with the following modifications: .5 gms. of theine was dissolved in water, a few drops of sulphuric acid added, and the volume made up to 250 cc; 50 cc. portions were taken for the determinations. Working in this way, the results were:

\*A portion of thesis, with additional determinations and literature, submitted to the Chemical Faculty of Cornell University for the Degree of Bachelor of Science, June, 1889.

†Fres. Zeit. 22, p. 379.

‡Fres. Zeit. 27, p. 222.

§J. Eng. Ch. Sci., June, 1889.

||J. Eng. Ch. Sci., June, 1889.

28.76	per cent. N
28.81	" "
28.79	" "
<hr/>	
Average, 28.79	" "

Some difficulty was found in determining the length of time necessary to carry on the digestion with sulphuric acid since the alkaloid dissolves in the acid, giving immediately a colorless solution. In the above determinations the digestion was carried on for an hour, after first evaporating the 50 cc. portions nearly to dryness.

From the results obtained, it is evident that the alkaloid, *theine*, yields all of its nitrogen to form ammonia, as do the protein compounds; and so in tea, the nitrogen obtained by the Kjeldahl method is the *total* alkaloid and albuminoid nitrogen present, and it only remains to separate and determine each.

The albuminoids in tea are almost entirely insoluble in hot water, as is shown by the analysis of Bell.\* Three samples of tea were taken and the following determinations made:

	Total N.	Insol. N.	Alb.* N.	Total N. Minus Insol. N.	Total N. Minus Alb. N.
Tea Dust . . . .	4.12	3.62	3.67	.50	.55
Black Tea . . . .	4.88	3.16	3.20	1.72	1.68
Japan Tea . . . .	4.39	2.83	2.85	1.56	1.54

This leaves for the alkaloid nitrogen when the albuminoid nitrogen, as thus determined, is taken from the total .55 per cent., 1.68 per cent. and 1.54 per cent. against .50 per cent., 1.72 per cent. and 1.56 per cent. when the insoluble nitrogen as determined is taken from the total.

The insoluble nitrogen was determined in the following way: About .8 gms. of the tea sample was weighed into a beaker, and boiled with about 20 cc. water, decanted, and boiled again, this being repeated four or five times with fresh portions of water.

The whole was then brought upon a Schleicher and Schull's No. 589 filter paper, and the filter and its contents put into the digestion flask. The whole amount of water used ought not to exceed 140 cc.

As a check upon the work, the determination of theine was

\*Stutzer's method.

tried by a number of methods (four in all), but with unsatisfactory results. The theine was either obtained in an impure state, or a loss would occur in the purification processes.

Tests were made, however, in the following ways :

1. A sample of tea was taken and the total nitrogen determined. To a weighed portion of this sample, a weighed quantity of theine was added, and the nitrogen again determined.

Total Nitrogen of leaf and alkaloid added . . . .	6.81	per cent.
Total Nitrogen of leaf . . . . .	4.44	"
Nitrogen from alkaloid added . . . . .	2.37	"
Calculated increase . . . . .	2.43	"

2. A sample of tea was exhausted and tannic acid added, and treated as above.

Total Nitrogen of exhausted leaf and alkaloid added	3.77	per cent.
Total Nitrogen of exhausted leaf . . . . .	2.36	"
Nitrogen from alkaloid added . . . . .	1.41	"
Nitrogen from calculated increase . . . . .	1.44	"

In order to insure success the following points must be observed:

1. The sulphuric acid digestion should be carried on until the contents of the flask are colorless.
2. The tea sample must be ground and prepared in the same way as the directions given for the preparation of fodder samples in Bulletin No. 24 A. O. A. C.
3. When the sample is thus prepared, the theine is readily removed by the treatment with boiling water, and too prolonged washing or boiling must be avoided.

This method for the determination of theine in tea has been tried upon a number of samples including Japan, Black and Dust tea, with additional determinations of tannin, ash, moisture and essential oil. The percentage of theine has ranged in "Dust tea" from .5 to 1.50 per cent., in the other samples from 2 to 4 per cent. and in each case where the theine has been found to be low, the tannin has been correspondingly low, although this would not be the case in samples of tea where tannin (which can be obtained so abundantly) has been added as an adulterant.

# THE ANALYSIS OF WATER TO DETERMINE SCALE-FORMING INGREDIENTS.\*

BY PROF. THOMAS B. STILLMAN.

The scale-forming ingredients of a water are usually composed of calcium and magnesium carbonates and calcium sulphate, and though an analysis of a water for boiler purposes usually states the number of grains per gallon of the above constituents, the analysis should also comprise the determination of many other ingredients, not scale forming, that are necessary to a proper estimation of the former.

This is especially true of the alkalies, which are not always determined in a commercial analysis for boiler purposes, the amounts of lime, magnesia, chlorine, carbonic and sulphuric acids being considered a sufficient index of the character of the water.

The alkalies and their salts rarely form scale in boilers,† and so cannot be classed as scale forming, yet they play fully as important a part in the relation they sustain to the sulphuric acid and chlorine.

If all the sulphuric acid in a water were combined with the alkalies, there would be no sulphate of lime present, and the latter would be eliminated as a part of the scale ingredients. This is a condition rarely occurring, however, since in most waters a portion of the sulphuric acid is united with the alkaline earths and the alkalies. The indirect estimation of the carbonic acid would be changed also. That is to say, where the  $\text{CO}_2$  is estimated by uniting all the  $\text{CaO}$  and  $\text{MgO}$  (left uncombined with the  $\text{SO}_3$  and  $\text{Cl}$ ) with  $\text{CO}_2$ , it is evident that if all the  $\text{SO}_3$  is united with  $\text{CaO}$ , when a large portion belonged to the alkalies, the amount of carbonate of lime would be too small, and also that the proportion of the  $\text{CO}_2$  would be deficient by the amount required to saturate the  $\text{CaO}$  incorrectly united with the  $\text{SO}_3$ .

There is nothing in the usual commercial analysis to indicate whether the sulphuric acid, as determined in the water, is all united with the lime to form calcium sulphate or not; but the

\*Stevens Indicator, October, 1890.

†A sample of scale, analyzed by the author in 1887, had the following composition :

Carbon . . . . .	1.01	MgCl . . . . .	1.71
SiO <sub>2</sub> . . . . .	1.52	CaCl <sub>2</sub> . . . . .	10.32
Al <sub>2</sub> O <sub>3</sub> . . . . .	0.43	CaSO <sub>4</sub> . . . . .	11.20
NaCl . . . . .	72.12	Undetermined . . . . .	0.68
KCl . . . . .	1.01		
			100.00

custom has been so to unite it ; with the result that calcium sulphate may be represented as a large component of the scale-forming material, when, in reality, none whatever may be present. The converse is also true. In a partial analysis of the Monongahela River water (Transactions American Institute of Mining Engineers, Vol, XVII., page 353), the amounts of objectionable substances, for boiler use, are given as follows :

Total lime . . . .	161	parts per 100,000 =	94	grains per gallon.
“ magnesia . . . .	33	“ “ =	19	“ “
Sulphuric acid . . .	210	“ “ =	122	“ “
Chlorine . . . . .	38	“ “ =	22	“ “

It states further the amounts of carbonates of lime and magnesia precipitated upon boiling to be :

Carbonate of lime . . .	130	parts per 100,000 =	76	grs. per gal.
“ magnesia, . . . .	21	“ “ =	12.2	“ “

The alkalis not having been determined, the proportion of sulphuric acid combined with lime becomes problematical ; in fact, the inference is that there is none present, when, in all probability, it amounts to a large percentage.

Another example (Report State Geologist New Jersey, 1885, page 121), as follows :

*Analysis of Water from Well No. 1.*

Total solids . . . . .	12.800	grains per gallon.
Chlorine, as chlorides . . . . .	2.2422	
Sulphuric acid, as sulphates . . .	0.3666	
Silica . . . . .	0.9098	
Iron and alumina . . . . .	0.0233	
Lime . . . . .	2.1461	
Magnesia . . . . .	0.3965	
	<hr/>	6.0845
Alkalies and undetermined matter . .		6.7155

*Analysis of Water from Well No. 2.*

Total solids . . . . .	12.1184	grains per gallon.
Chlorine, as chlorides . . . . .	1.1955	
Sulphuric acid, as sulphates . . .	0.3091	
Silica . . . . .	0.5948	
Iron and alumina . . . . .	0.0233	
Lime . . . . .	3.7907	
Magnesia . . . . .	0.6531	
	<hr/>	6.5665
Alkalies and undetermined matter . .		5.5519



Numerous instances are constantly being cited in the literature of technical water analysis of similar incomplete analyses, and having thus indicated the necessity of including the alkalies, the accompanying scheme has been arranged to show the method of making a water analysis for boiler purposes.

To show, in detail, the method of using the scheme, the following water analysis is given. (Preliminary tests having shown the water to contain but little residue, 8 liters of it were evaporated.)

Pt. capsule and residue (8 liters) . . . . .	147.460 grammes.	
"    without residue . . . . .	146.620	"
Total residue . . . . .	0.840	"
Before ignition, capsule and residue . . . . .	147.460	"
After " " " " . . . . .	147.197	"
Organic, volatile (CO <sub>2</sub> , etc.) . . . . .	.263	
SiO <sub>2</sub> + crucible . . . . .	15.970	
Crucible. . . . .	15.904	
SiO <sub>2</sub> . . . . .	.066	

Solution made to 100 cc. — 75 cc. for bases., 25 cc. for SO<sub>3</sub>.

75 cc.	SO <sub>3</sub>
Fe <sub>2</sub> O <sub>3</sub> (Al <sub>2</sub> O <sub>3</sub> ) + crucible . . 15.9338	Crucible and BaSO <sub>4</sub> . . . . 16.023
crucible . . 15.903	Crucible. . . . . 15.903
.0308	BaSO <sub>4</sub> . . . . . .120
CaO + crucible . . . . . 16.0197	
Crucible . . . . . 15.903	
CaO . . . . . .1167	
MgO + crucible . . . . . 15.928	
Crucible . . . . . 15.903	
MgO. . . . . .025	

The chlorine found by titration amounted to 0.0055 grammes per liter or 0.32 grains per gallon.

Pt. dish and alkaline sulphates and (MgSO <sub>4</sub> ) . . .	53.370 gms.
Pt. dish . . . . .	53.197 "
Sulphates . . . . .	.173 "

Dissolved in H<sub>2</sub>O, made solution up to 50 cc.; 25 cc. for magnesia determination, and 25 cc. for potash determination.



*Table for Converting Milligrammes per Liter into Grains per U. S. Gallon of 231 Cubic Inches.*

Milligrams per liter.	Grains per Gallon.	Milligrams per liter.	Grains per Gallon.
1 . . . . .	= 0.0583	51 . . . . .	= 2.9742
2 . . . . .	" 0.1160	52 . . . . .	" 3.0325
3 . . . . .	" 0.1749	53 . . . . .	" 3.0908
4 . . . . .	" 0.2332	54 . . . . .	" 3.1491
5 . . . . .	" 0.2915	55 . . . . .	" 3.2074
6 . . . . .	" 0.3499	56 . . . . .	" 3.2658
7 . . . . .	" 0.4082	57 . . . . .	" 3.3241
8 . . . . .	" 0.4665	58 . . . . .	" 3.3824
9 . . . . .	" 0.5248	59 . . . . .	" 3.4407
10 . . . . .	" 0.5831	60 . . . . .	" 3.4990
11 . . . . .	" 0.6414	61 . . . . .	" 3.5573
12 . . . . .	" 0.6998	62 . . . . .	" 3.6157
13 . . . . .	" 0.7581	63 . . . . .	" 3.6740
14 . . . . .	" 0.8165	64 . . . . .	" 3.7323
15 . . . . .	" 0.8747	65 . . . . .	" 3.7906
16 . . . . .	" 0.9330	66 . . . . .	" 3.8489
17 . . . . .	" 0.9914	67 . . . . .	" 3.9073
18 . . . . .	" 1.0497	68 . . . . .	" 3.9656
19 . . . . .	" 1.1080	69 . . . . .	" 4.0239
20 . . . . .	" 1.1663	70 . . . . .	" 4.0822
21 . . . . .	" 1.2246	71 . . . . .	" 4.1405
22 . . . . .	" 1.2829	72 . . . . .	" 4.1988
23 . . . . .	" 1.3413	73 . . . . .	" 4.2572
24 . . . . .	" 1.3996	74 . . . . .	" 4.3155
25 . . . . .	" 1.4579	75 . . . . .	" 4.3738
26 . . . . .	" 1.5162	76 . . . . .	" 4.4321
27 . . . . .	" 1.5745	77 . . . . .	" 4.4904
28 . . . . .	" 1.6329	78 . . . . .	" 4.5488
29 . . . . .	" 1.6912	79 . . . . .	" 4.6071
30 . . . . .	" 1.7495	80 . . . . .	" 4.6654
31 . . . . .	" 1.8078	81 . . . . .	" 4.7237
32 . . . . .	" 1.8661	82 . . . . .	" 4.7820
33 . . . . .	" 1.9244	83 . . . . .	" 4.8403
34 . . . . .	" 1.9828	84 . . . . .	" 4.8987
35 . . . . .	" 2.0411	85 . . . . .	" 4.9570
36 . . . . .	" 2.0994	86 . . . . .	" 5.0153
37 . . . . .	" 2.1576	87 . . . . .	" 5.0736
38 . . . . .	" 2.2160	88 . . . . .	" 5.1319
39 . . . . .	" 2.2745	89 . . . . .	" 5.1903
40 . . . . .	" 2.3327	90 . . . . .	" 5.2486
41 . . . . .	" 2.3910	91 . . . . .	" 5.3069
42 . . . . .	" 2.4493	92 . . . . .	" 5.3652
43 . . . . .	" 2.5076	93 . . . . .	" 5.4235
44 . . . . .	" 2.5659	94 . . . . .	" 5.4818
45 . . . . .	" 2.6243	95 . . . . .	" 5.5402
46 . . . . .	" 2.6826	96 . . . . .	" 5.5984
47 . . . . .	" 2.7409	97 . . . . .	" 5.6568
48 . . . . .	" 2.7992	98 . . . . .	" 5.7151
49 . . . . .	" 1.8575	99 . . . . .	" 5.7734
50 . . . . .	" 2.9159	100 . . . . .	" 5.8318

The amounts obtained being :

Silica . . . . .	0.4771 grains per gallon.		
SO <sub>3</sub> . . . . .	1.2012	"	"
Cl . . . . .	0.3206	"	"
K <sub>2</sub> O . . . . .	0.0291	"	"
Na <sub>2</sub> O . . . . .	0.3615	"	"
MgO . . . . .	0.4490	"	"
CaO . . . . .	1.1313	"	"
Fe <sub>2</sub> O <sub>3</sub> Al <sub>2</sub> O <sub>3</sub> . . . . .	0.2973	"	"
Organic . . . . .	1.1254	"	"
Carbonic acid . . . . .	0.7989	"	"
	<hr/>		
	6.1914	"	"
Oxygen in excess of Cl . . . . .	0.0932	"	"
	<hr/>		
	6.0982	"	"

Having determined the component parts of the water residue in grains per gallon, it becomes necessary to unite these in chemical union, as nearly as possible, as they exist in the water.

The general rule may be stated as follows: The chlorine is combined with the sodium, if still in excess, then with the potassium, magnesium, and finally calcium. The sulphuric acid to the alkalis, provided there is not enough chlorine to saturate them, then to the calcium, and finally to the magnesium.

The carbonic acid is united with the calcium and magnesium after the other combinations are made. There are exceptions to this rule, mineral waters and many artesian well waters forming notable examples.

Carrying out the above, the following is obtained :

	Grams per liter.	Grains per gallon.
NaCl . . . . .	0.0091	0.5306
Na <sub>2</sub> SO <sub>4</sub> . . . . .	0.0033	0.1923
K <sub>2</sub> SO <sub>4</sub> . . . . .	0.0009	0.0524
CaSO <sub>4</sub> . . . . .	0.0311	1.8136
CaCO <sub>3</sub> . . . . .	0.0118	0.6880
MgCO <sub>3</sub> . . . . .	0.0162	0.9446
Fe <sub>2</sub> O <sub>3</sub> Al <sub>2</sub> O <sub>3</sub> . . . . .	0.0051	0.2973
SiO <sub>2</sub> . . . . .	0.0082	0.4771
Organic, etc. . . . .	0.0193	1.1254
	<hr/>	
Total . . . . .	0.1050	6.1213

# **SCHEME FOR WATER ANALYSIS.**

BY PROF. THOMAS B. STILLMAN.

Evaporate two liters of the water in a weighed platinum capsule, upon a water bath, to dryness; transfer to a hot-air bath and heat at 105° C. for 30 minutes; cool and weigh. Ignite slowly to a dull red heat until all carbonaceous matter is consumed; cool and weigh. The loss of weight equals organic and volatile matter. Warm the contents of the capsule with 10 cc. to 15 cc. of HCl, add 25 cc. H<sub>2</sub>O, boil and filter through an ashless filter into a 100 cc. graduated flask; wash thoroughly, make contents of flask to containing mark with H<sub>2</sub>O; mix well.

<p>(1) <i>Residue</i>: Consists of insoluble mineral matter — <math>\text{SiO}_2</math> or <math>\text{SiO}_2.\text{Al}_2\text{O}_3</math> (<math>\text{CaSO}_4</math>). It should be dried, ignited and weighed; then fused with <math>\text{Na}_2\text{CO}_3</math> in platinum crucible, dissolved in <math>\text{H}_2\text{O}</math>, made acid with <math>\text{HCl}</math>, evaporated to dryness with <math>\text{HCl}</math>, taken up with <math>\text{H}_2\text{O} + \text{HCl}</math> and filtered.</p> <p><i>Filtrate</i>: Make alkaline with <math>\text{NH}_4\text{HO}</math>, boil and filter.</p> <p><i>Residue</i>: <math>\text{SiO}_2</math>; ignite and weigh as <math>\text{SiO}_2</math>.</p>	<p><i>Filtrate</i>: Add solution of <math>\text{NH}_4\text{O}</math>; set aside 3 hours, then filter.</p> <p>(6) <i>Filtrate</i>: Evaporate to dryness in platinum dish; ignite to expel all ammonia salts; cool, add water, boil and filter; wash well.</p> <p>(7) <i>Residue</i>: Consists of <math>\text{MgO}</math>, <math>\text{HO}</math>. Dry, ignite, and weigh as <math>\text{MgO}</math>.</p>	<p>(2) <i>Solution</i>: 100 cc. Divide into two portions, one of 75 cc. for bases and one of 25 cc. for <math>\text{SO}_4</math>. 75 cc.: Make alkaline with <math>\text{NH}_4\text{HO}</math>, boil and filter (all weights obtained to be divided by 3 and multiplied by 4).</p> <p>(3) <i>Residue</i>: Consists of <math>\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3</math>. Dry, ignite, and weigh as such.</p> <p>(4) <i>Filtrate</i>: Add solution of <math>\text{NH}_4\text{O}</math>; set aside 3 hours, then filter.</p> <p>(5) <i>Residue</i>: Consists of <math>\text{CaO}</math>. Dry, ignite, and weigh as <math>\text{CaO}</math>.</p>	<p>(8) Transfer to a weighed platinum dish, and add a few drops of <math>\text{H}_2\text{SO}_4</math>; evaporate to dryness, and ignite to constant weight. This residue is composed of <math>\text{Na}_2\text{SO}_4</math>, <math>\text{MgSO}_4</math>, (<math>\text{K}_2\text{SO}_4</math>); after weighing, dissolve in <math>\text{H}_2\text{O}</math>, make solution up to 50 cc.; mix thoroughly, and divide into 2 equal portions of 25 cc. each.</p> <p>1st, 25cc.: Add a few drops of <math>\text{HCl}</math>, then solution of <math>\text{NH}_4\text{HO}</math>; then add, with constant stirring, solution of some alcohol. <math>\text{Na}_2\text{HPO}_4</math>; set aside 3 hours, filter, dry, ignite on small tared filters, and weigh as dry and weigh as <math>\text{Mg}_2\text{P}_2\text{O}_7</math>; calculate this <math>\text{K}_2\text{PtCl}_6</math>. Calculate to <math>\text{MgSO}_4</math>, and subtract, this weight to <math>\text{K}_2\text{SO}_4</math>, after multiplying by 2, and subtract, from total weight of multiplying by 2, from sulphates in (8), and weight of <math>\text{Na}_2\text{SO}_4</math> and <math>\text{K}_2\text{SO}_4</math>, and the residue left will be the weight of <math>\text{Na}_2\text{SO}_4</math>. The <math>\text{K}_2\text{SO}_4</math> and <math>\text{Na}_2\text{SO}_4</math> are then calculated to <math>\text{K}_2\text{O}</math> and <math>\text{Na}_2\text{O}</math>.</p> <p>2d, 25cc.: Add a few drops of <math>\text{HCl}</math>, then solution of <math>\text{PCl}_4</math>. Evaporate on water bath, then add, with constant stirring, solution of some alcohol. <math>\text{Na}_2\text{HPO}_4</math>; set aside 3 hours, filter, dry, ignite on small tared filters, and weigh as dry and weigh as <math>\text{Mg}_2\text{P}_2\text{O}_7</math>; calculate this <math>\text{K}_2\text{PtCl}_6</math>. Calculate to <math>\text{MgSO}_4</math>, and subtract, this weight to <math>\text{K}_2\text{SO}_4</math>, after multiplying by 2, and subtract, from total weight of multiplying by 2, from sulphates in (8), and weight of <math>\text{Na}_2\text{SO}_4</math> and <math>\text{K}_2\text{SO}_4</math>, and the residue left will be the weight of <math>\text{Na}_2\text{SO}_4</math>. The <math>\text{K}_2\text{SO}_4</math> and <math>\text{Na}_2\text{SO}_4</math> are then calculated to <math>\text{K}_2\text{O}</math> and <math>\text{Na}_2\text{O}</math>.</p>	<p>25 cc.: Warm, add solution of barium chloride, and allow to settle 3 hours; filter, wash, dry, ignite, and weigh as <math>\text{BaSO}_4</math>. Calculate <math>\text{SO}_4</math>, and multiply result by 4.</p>	<p><math>\text{CO}_2</math>: Is found by combining the chlorine and sulphuric acid with the bases, then determining how much <math>\text{CO}_2</math> is required to convert the rest of the <math>\text{CaO}</math> and <math>\text{MgO}</math> to carbonates, as shown in the example given below.</p> <p><math>\text{Cl}</math>: Concentrate 250 cc. of the water in a porcelain dish to about 50 cc. Add a few drops of <math>\text{K}_2\text{CrO}_7</math> sol., and titrate with a standard solution of <math>\text{AgNO}_3</math>, in which each cc. corresponds to 0.007 gm. of chlorine. Multiply result by 4 = gms. of <math>\text{Cl}</math> per liter.</p>		
$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3$	(Sol.) $\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3$	$\text{CaO}$ .	$\text{MgO}$ .	$\text{SO}_4$ .	$\text{CO}_2$ .	$\text{Cl}$ .

This analysis shows that the principal scale-forming ingredient is calcium sulphate, being more than equal to the carbonates of calcium and magnesium.

The following analysis is of a water containing sulphuric acid, but the alkalis being present in sufficient amount to combine with all of it, as well as the chlorine, no sulphate of lime is present.

	Grams per liter.	Grains per gallon.
SiO <sub>2</sub> . . . . .	0.0038	0.2215
SO <sub>3</sub> . . . . .	0.0110	0.6414
Cl . . . . .	0.0062	0.3615
K <sub>2</sub> O . . . . .	0.0033	0.1923
Na <sub>2</sub> O . . . . .	0.0185	1.0788
MgO . . . . .	0.0165	0.9388
CaO . . . . .	0.0466	2.7175
Al <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> . . . . .	0.0020	0.1166
Organic . . . . .	0.0246	1.4345
Carbonic acid . . . . .	0.0530	3.0908
	<hr/>	<hr/>
	0.1851	10.7937
Oxygen in excess of Cl . . . . .	0.0021	0.1224
	<hr/>	<hr/>
Total . . . . .	0.1830	10.6713

Combined as follows :

NaCl . . . . .	0.0154	0.8900
Na <sub>2</sub> SO <sub>4</sub> . . . . .	0.0141	0.8223
K <sub>2</sub> SO <sub>4</sub> . . . . .	0.0061	0.3557
CaCO <sub>3</sub> . . . . .	0.0833	4.8577
MgCO <sub>3</sub> . . . . .	0.0338	1.9710
Al <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> . . . . .	0.0020	0.1166
SiO <sub>2</sub> . . . . .	0.0038	0.2215
Organic . . . . .	0.0246	1.4345
	<hr/>	<hr/>
Total . . . . .	0.1831	10.6773

Where all the chlorine is not in combination with the sodium and potassium, chloride of magnesium is usually present.

This latter compound, while not scale-forming, is considered as an active, corrosive agent—upon the supposition that at the temperature of 100° C., and higher, it is decomposed, and hydrochloric acid formed and liberated—consult *Journal Society of Chemical Industry*, Vol. IX, p. 472 ; also, *Treatise on Steam Boilers*, by Wilson, p. 168.

The report, given below, is of a water from a driven well in Florida. Complaint having been made that not only was the scale excessive in amount, but that corrosive action was also very marked, an analysis was made; reference to which readily explains the difficulty encountered in the boilers.

NaCl . . . . .	0.323	gms. per liter.	18.87	grains per gallon.
KCl. . . . .	0.067	" "	3.91	" "
MgCl <sub>2</sub> . . . . .	0.104	" "	6.06	" "
CaSO <sub>4</sub> . . . . .	0.197	" "	11.52	" "
CaCO <sub>3</sub> . . . . .	0.293	" "	17.10	" "
MgCO <sub>3</sub> . . . . .	0.144	" "	8.40	" "
SiO <sub>2</sub> . . . . .	0.011	" "	0.62	" "
Al <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> . . .	0.007	" "	0.46	" "
Organic. . . . .	0.138	" "	8.02	" "
Total . . . . .	1.284	" "	74.86	" "

In all of the above analyses the constituents have been stated in grains per gallon, rather than in parts per 100,000, the former being in general use by the mechanical profession as the proper method by which to express the weights of the component parts of a water.

## ABSTRACTS.

### INORGANIC ANALYSIS.

**Effect of Temperature upon the Determination of Ammonia by Nesslerisation.**—Allen Hazen and Harry W. Clark, Chem. News **62**, 125, (American Chem. Journal XII, No. 6).

It was found by experiments that the color obtained by Nesslerising an ammonia solution varied with the temperature, the warmer the solution, the deeper the color. A standard containing 4 cc. of ammonia solution Nesslerised at 30° will give a color equal to that obtained from 5 cc., Nesslerised at 15°, or 6 cc. Nesslerised at 0°, but a change in temperature, after Nesslerising, will not change the color very much. Hence the importance of bringing standards and distillates to the same temperature before Nesslerising, in order to obtain accurate results. A. H. W.

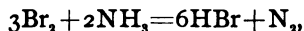
**Volumetric Determination of Nitrogen.**—J. H. Smith, Chem. Zeit. 14, 1223.

The method is based upon the following reactions :

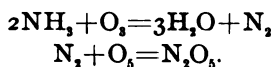
1st, That potassium permanganate liberates free bromine from an alkaline bromide in an acid solution.



2d. That this bromine oxidizes nitrogenous compounds, liberating free nitrogen,



or by complete oxidation converts the nascent nitrogen into nitric acid.



The author has experimented with ammonia salts, cyanides, urea, and albumen with more or less satisfactory results, but the method is not at present ready for practical use. s. c.

**Determination of Nitrates in Fertilizers.**—T. F. Schmitt, Chem. Zeit. 14, 1410.

40 cc. glacial acetic acid is poured into a 750 cc. Erlenmeyer flask, and to it are added 15 gms. of a mixture of equal parts zinc dust and iron filings. After shaking, 50 cc. (= ½ gm. substance) of an aqueous solution of the nitrate is poured in, and the contents of the flask well mixed. At the end of 15 minutes, 15 gms. of the iron and zinc mixture are again added, and to prevent solidification of the mixture, 30 cc. of water is poured into the flask and the contents are thoroughly mixed by shaking. At the end of 30 or 40 minutes, the nitrates are completely reduced to ammonia, which is distilled off and determined as in Kjeldahl's method. The temperature of the solution during the reduction should not exceed 75° or 80°, since the ammonium acetate begins to decompose at 89°; and enough caustic soda solution should be added to the distilling flask to re-dissolve the zinc hydrate formed. The results obtained are accurate. s. c.

**The Estimation of Nitrites in Potable Waters.**—John C. Thresh, Chem. News 62, 203. (From the Pharmaceutical Era, Sept. 20, 1890.)

The reagents employed are :



## 1. Solution of starch and potassium iodide.

Starch in powder . . . . .	0.2 gms.
Caustic potash . . . . .	1.0 "
Potassium iodide . . . . .	2.0 "
Water . . . . .	200 cc.

Add the starch to 10 cc. of the water, and when uniformly mixed, add the caustic potash, dissolve in the cold, and add the rest of the water and the potassium iodide, strain or filter. This solution will remain unchanged for months, and 1 cc. is required for a determination.

2. Dilute sulphuric acid. 1 part sulphuric acid, 3 parts water.

3. Solution of sodium nitrite. 0.493 gms. sodium nitrite dissolved in 11 oz. of water (1 cc.=0.1 mg. N.).

To carry out the process, first shake well the sample of water in a bottle partly filled to saturate with air; put 50 cc. into a Nessler cylinder, add 1 cc. of the starch and iodide solution, then 1 cc. of the dilute acid, and stir. Assuming the temperature at 60° F., the immediate appearance of a dark-blue tint indicates that the water contains more than 1 part per million of nitrous nitrogen. If it becomes blue after a few seconds, it contains about 0.1 part per million; if after 10 seconds, less than the amount. When the blue color appears instantly, the sample must be diluted with known proportions of nitrite free water (saturated with air) until it is found that it takes the color several seconds to develop. A standard solution of sodium nitrite is now made by diluting 1 cc. of the stronger solution with 200 cc. of water. 1 cc. of the weaker solution, diluted to 50 cc., represents 0.01 mg. nitrous nitrogen per L. Measure into Nessler glasses varying amounts of this standard solution, and fill up with water. Take 50 cc. of the sample, add successively 1 cc. of the starch and iodide solution and dilute acid, and note the color. The time occupied in a determination is stated as usually five minutes. A. H. W.

**Estimation of Nitrogen in Chili Saltpeter.**—O. Foerster, Chem. Zeit. 14, 509.

2 or 3 gms. of the sample is fused in a weighed porcelain crucible with lid. After cooling, 25 cc. hydrochloric acid (3 parts acid to 1 part water) is added, and the solution evaporated to dryness. This treatment is repeated twice to expel all the nitric

acid, and the final residue is heated for some time at 150 degrees, and then to dull redness, after which it is cooled in a desiccator and weighed. The difference in weight represents the loss by exchanging a molecule of  $\text{NO}_2$  for an atom of chlorine, which would be to the atomic weight of nitrogen as 1 : x.

$$*(61.89 - 35.32) : 14.01 = 1 : .52828$$

This method cannot be used in presence of magnesium chloride since this substance loses hydrochloric acid in drying. s. c.

**On the Determination of Oxygen in the Air.**—J. Alfred Wanklyn and W. J. Cooper, *Chem. News*, **62**, 155.

The old process of Priestley and Cavendish is slightly altered by the authors. In brief, their method is to measure the sample of air and the nitric oxide, used as the reagent, separately. When the two are brought together in the presence of water, there is at once reaction, and the resultant ruddy fumes are absorbed rapidly by the water, and a second reading is taken. One-third of the contraction is the volume of the oxygen in the air. Details are given in "Air Analysis," recently published, by the above chemists.

A. H. W.

**Determination of Free and Combined Carbonic Acid in Water.**—E. Jelowetz, *Chem. Zeit. Rep.* **14**, 259.

500 cc. of the water to be analyzed is placed in a flask connected with the usual drying tubes and potash bulb for purifying and collecting carbon dioxide, and to it is added 5 cc. of concentrated calcium chloride solution free from carbonate. The mixture is then boiled, which liberates all the free and half combined acid. After the carbon dioxide has been absorbed the potash bulb is weighed and again attached to the apparatus. Dilute acid is then run into the flask and combined carbon dioxide is determined in the usual way.

s. c.

**Estimation of Zinc and Nitrogen in Impregnated Railroad Ties.**—A. Grittner, *Ztschr. angew. Chem.* 1890, 386.

For Zn two methods are available—first, to fuse the borings from the wood with  $\text{Na}_2\text{CO}_3 + \text{KNO}_3$  and treating the fused mass with acetic acid, filtering, and precipitating the Zn in the filtrate; the second method being to burn the wood borings directly and

\*"Revised Atomic Weights," L. Meyer, and K. Seubert.

treat the ash with acetic acid, filtering, and precipitating the Zn in the filtrate by means of sulphuretted hydrogen. The nitrogen is to be determined by the Kjeldahl-Willfahrt method, which, with woods, gives very good results.

J. E. W.

**Determination of Metallic Zinc in Zinc Dust.**—W. Minor. *Chem. Zeit.* **14**, 1142.

The author describes a modification of Drewsen's method as follows:—30 gms. pure crystallized potassium bichromate are dissolved in water, filtered, and diluted to one liter. A solution of ferrous ammonium sulphate is made by dissolving 150 gms. ferrous sulphate and 75 gms. ammonium sulphate in water, adding 100 cc. concentrated sulphuric acid, and diluting to one liter. The chromate solution is standardized for zinc by adding one gram of pure zinc to a measured quantity of the solution and adding, drop by drop, 20 cc. dilute sulphuric acid. In twenty minutes the action has ceased and the excess of bichromate is then titrated with the standard ferrous ammonium sulphate solution using potassium ferricyanide as an indicator. The ferrous sulphate solution is standardized in the usual manner, against the chromate solution.

The analysis is performed in the same way by substituting zinc dust for the pure zinc in the above description. The author finds that this gives inaccurate results owing to the presence of cadmium and iron in a metallic state which are determined as zinc. They must be determined separately and deducted from first result which will give the amount of metallic zinc.

S. C.

**Determination of Zinc in Siliceous Ores Containing Lead.**—W. Minor, *Chem. Zeit.* **14**, 1003.

2 gms. of the ore are boiled for 15 minutes with 60 cc. of weak soda solution. After pouring off the supernatant liquid, the residue is again boiled with soda. This operation is repeated a third time and the solution filtered. The lead is then separated from the filtrate by acidifying with sulphuric acid, and diluting to a known bulk. After standing a few hours, half the volume is filtered off, mixed with an excess of ammonia, and titrated with sodium sulphide. No notice is taken of the slight precipitate of alumina that forms on the addition of ammonia. By this method

only the zinc that is combined as carbonate and silicate is determined, and not that combined as sulphide. S. C.

**The Determination of Phosphoric Acid in Basic Slags.**—G. Arth, Chem. News **62**, 155. ("Annalen der Chemie.")

On analyzing a basic slag, containing 13.85 per cent. phosphoric acid, after separating silica and while evaporating the filtrate with nitric acid to expel the chlorine, the author made the following observation: When the hydrochloric acid was nearly driven off, a granular, yellow precipitate formed in the concentrated liquid, which gradually increased, and which was insoluble in nitric acid, cold or hot, dilute or concentrated, and as this precipitate contained phosphoric acid, it is impossible to have a nitric solution containing all the phosphorus. This yellow precipitate, after drying at  $100^{\circ}$ – $105^{\circ}$ , was found to have the formula  $\text{Fe}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ , and was soluble in strong hydrochloric acid. Although the composition of this phosphate is the same as the ordinary precipitated phosphate, the latter is nearly white and easily soluble in the mineral acids. When treated with cold potash lye, these allotropic phosphates exhibit different degrees of solubility and yield two oxides, the appearance of which is decidedly different, but the filtrate contains the phosphoric acid. This new ferric phosphate may be easily prepared from pure ferric chloride and disodium phosphate, by evaporating the solution with a sufficient excess of nitric acid, and in analytical operations, as in the case of basic slags, where the ferric oxide and phosphoric acid are in certain proportions, the compound may be formed. Another tetrahydrated ferric phosphate of a rosy white color, insoluble in nitric acid, is sometimes formed when a mixture of ferric chloride, disodium, phosphate, and nitric acid are evaporated, and this may be the compound obtained by Erlenmeyer under different conditions. A. H. W.

**Separation of Copper from Arsenic by Electrolysis.**—LeRoy W. McCay, Chem. Zeit. **14**, 509.

By using an ammoniacal solution of copper to which an alkaline arsenate had been added, the author effected a complete separation of copper which contained no traces of arsenic. A current from 4 to 6 Meidinger's elements was used and the time required

was 24 hours. No injurious effect was produced by allowing the current to run after the copper was all deposited. A number of results accompany the article. S. C.

**Electro-Deposition of Silver.**—S. Ernest. Chem. News. **62**, 137.

In order to obtain a conducting surface on plaster casts, for subsequent coating with copper by electrical deposits, the author obtained a finely divided deposit of silver in the following way. The cast was first moistened with water, then brushed over with a solution of silver nitrate, when it was allowed to come in contact with antimonuretted or arseniuretted hydrogen, when an instant deposit of  $\text{Ag}_3\text{Sb}$  or  $\text{Ag}_3\text{As}$  was formed, an excellent conductor.

A. H. W.

**Electrolysis of Different Substances.**—P. L. Aslanoglon, Chem. News **62**, 42.

1. Water. On passing a current of electricity from six Fuller's mercury bichromatic cells through ordinary London tap water for about twelve hours a white deposit appeared on the hydrogen pole, which on analysis was found to be calcium carbonate. The oxygen pole was free from any deposit.

2. Magnesium carbonate was suspended in distilled water, and carbon dioxide passed through the solution, which was then filtered. A white deposit appeared on the hydrogen pole, while the oxygen was free from any solid matter.

3. Silver chloride dissolved in sodium thiosulphate, filtered, and electrolysed, gave a thick grey deposit, turning at once to black on the hydrogen pole, while the odor of sulphuretted hydrogen was observed. The black precipitate, on examination, was found to be very fine metallic silver.

4. Lead sulphate was dissolved in a solution of tartaric acid, neutralized with ammonia, and filtered. The hydrogen pole, on passing the current, was coated with a black deposit which smelled of ammonia, while the oxygen pole was coated a golden yellow, and in a few hours the solution assumed the same color, but gradually darkened.

5. Barium carbonate and strontium carbonate, treated similarly to the magnesium carbonate, gave white precipitates on the hydrogen pole.

6. When zinc carbonate was treated in like manner, the hydrogen pole was coated with a greyish-black residue of zinc carbonate, while the liquid became turbid, a gelatinous precipitate floated on the surface, and by shaking the tube, the precipitate fell to the bottom.

7. A mixture of ferrous sulphate and sodium carbonate were placed in a flask of distilled warm water, and  $\text{CO}_2$  was passed through for half an hour. After settling and pouring off the supernatant liquid, fresh hot distilled water was added,  $\text{CO}_2$  was passed for half an hour, and this operation was repeated six times,  $\text{CO}_2$  being passed through the flask meanwhile to prevent oxidation of the iron. The last time it was allowed to settle a few hours and rapidly filtered into the electrolysis tube, when the liquid was quite clear and free from any signs of oxidation. On electrolysing, there were no deposits on either pole A. H. W.

**Blowpipe Test for Mercury.**—T. Charlton, Chem. News 62, 41.

The author used Johnstone's test (Chem. News 59, 221; this Journal 3, 323), modified by adding a grain of iodine to the warm tube after the sublimate has been obtained. If there is not heat sufficient to volatilize the iodine, a gentle heat is applied, and when the vapors of iodine come in contact with the mercury sublimate, the characteristic bright scarlet mass is formed.

A. H. W.

## ATOMIC WEIGHTS.

EDITED BY F. W. CLARKE.

**Fluorine.**—Atomic weight redetermined by Moissan, who operated by the old method of converting fluorides into sulphates. The detailed weighings are not published.

Ratio, $2\text{NaF} : \text{Na}_2\text{SO}_4$ .	5 experiments.	F = 19.04 to 19.08.
" $\text{CaF}_2 : \text{CaSO}_4$ .	4 "	19.02 " 19.08.
" $\text{BaF}_2 : \text{BaSO}_4$ .	5 "	19.05 " 19.09.

Calculated with  $\text{O} = 16$ ,  $\text{Na} = 23.05$ ,  $\text{S} = 32.074$ .

The assumed values for Ca and Ba are not given. The fluorides were prepared from specially purified materials.—*Comptes Rendus* 111, 570.

**Oxygen.**—Noyes has continued his work upon the atomic weight of oxygen, employing the method already noticed in this Journal (1889, 3, 349). Four series of results are given, as follows :

1	2	3	4
15.885	15.898	15.891	15.898
15.882	15.932	15.885	15.896
15.909	15.913	15.898	15.896
15.904	15.879	15.884	15.890
15.909	15.876	15.891	15.892
15.895	15.885	15.887	15.885
Mean, 15.8973	15.8971	15.8893	15.8929
$\pm .0032$	$\pm .0064$	$\pm .0014$	$\pm .0013$

*Am. Chem. Journ.* 12, 441.

**Glucinum.**—The atomic weight of this metal has been redetermined by Krüss and Moraht. (Ber. 23, 2552.)

The crystallized sulphate was ignited, and the residual oxide determined.

Percentage of  $\text{GlO}$  in  
 $\text{GlSO}_4 \cdot 4\text{H}_2\text{O}$ .

14.160  
14.161  
14.136  
14.143  
14.137  
14.146  
14.145  
14.143  
14.135  
14.146  
14.134  
14.155  
14.133  
14.154  
14.130  
14.153

Mean, 14.144

From 5 to 22 gms. of the sulphate were used in each experiment. In sum, if  $\text{O}=16$ , the authors find  $\text{Gl}=9.054$ ; but they do not state what value is assigned to S in their calculations.

**Manganese.**—Atomic weight redetermined by Weeren. (Inaugural Dissertation, Halle, 1890.)

Two methods employed, vacuum weight given throughout. First, conversion of  $\text{MnO}$  into  $\text{MnSO}_4$ .

15.2359 gms. $\text{MnO}$ gave	32.4142 $\text{MnSO}_4$ .	$\text{Mn} = 54.870$
13.9686     "     "	29.7186     "     "	54.867
13.7471     "     "	29.2493     "     "	54.859
15.5222     "     "	33.0246     "     "	54.865
14.9824     "     "	31.8755     "     "	54.867
14.6784     "     "	31.2304     "     "	54.861
<hr/> 88.1346	<hr/> 187.5126	<hr/> 54.865

Calculated with  $\text{O} = 15.96$ , and  $\text{S} = 31.98$ .

*Second Method:* Reduction of  $\text{MnSO}_4$  to  $\text{MnS}$  by heating in a stream of  $\text{H}_2\text{S}$ . This was von Hauer's method.

16.0029 gms. $\text{MnSO}_4$ gave	9.2228 $\text{MnS}$ .	$\text{Mn} = 54.860$
16.3191     "     "	9.4048     "     "	54.855
15.9307     "     "	9.1817     "     "	54.871
15.8441     "     "	9.1315     "     "	54.865
16.2783     "     "	9.3819     "     "	54.868
17.0874     "     "	9.8477     "     "	54.857
<hr/> 97.4625	<hr/> 56.1704	<hr/> 54.863

**Cadmium.**—Partridge, starting with cadmium purified by distillation in vacuo, has determined its atomic weight by three methods. First, cadmium oxalate was ignited to oxide.

1.09898 oxalate gave	.70299 $\text{CdO}$ .	$\text{Cd} = 111.819$
1.21548     "     "	.77746     "     "	111.793
1.10711     "     "	.70807     "     "	111.755
1.17948     "     "	.75440     "     "	111.780
1.16066     "     "	.74237     "     "	111.783
1.17995     "     "	.75471     "     "	111.783
1.34227     "     "	.85864     "     "	111.829
1.43154     "     "	.91573     "     "	111.823
1.53510     "     "	.98197     "     "	111.821
1.41311     "     "	.90397     "     "	111.834
<hr/> 12.66368	<hr/> 8.10031	<hr/> (111.8027)

**Terbium and Gadolinium.**—According to Boisbaudran, the atomic weight of terbium is 159.01 to 159.95. That of gadolinium is 155.53 to 156.12.—*Comptes Rendus* 111, pp. 409 and 474.



Second, cadmium sulphate was reduced to sulphide by heating in a stream of  $H_2S$ .

1.60514	sulphate gave	1.11076	CdS.	Cd =	111.793
1.55831	"	1.07834	"	"	111.789
1.67190	"	1.15669	"	"	111.790
1.66976	"	1.15554	"	"	111.818
1.40821	"	.97450	"	"	111.801
1.56290	"	1.08156	"	"	111.806
1.63278	"	1.12985	"	"	111.778
1.58270	"	1.09524	"	"	111.797
1.53873	"	1.06481	"	"	111.796
1.70462	"	1.17962	"	"	111.801
<hr/>		<hr/>		<hr/>	
15.93505		11.02691		(111.7969)	

In the third series of experiments, cadmium oxalate was reduced to sulphide in the same way.

1.57092	oxalate gave	1.13065	CdS.	Cd =	111.812
1.73654	"	1.24979	"	"	111.786
2.19276	"	1.57825	"	"	111.824
1.24337	"	.89492	"	"	111.823
1.18743	"	.85463	"	"	111.807
1.54038	"	1.10858	"	"	111.771
1.38905	"	.99974	"	"	111.806
2.03562	"	1.46517	"	"	111.833
2.03781	"	1.46658	"	"	111.774
1.91840	"	1.38075	"	"	111.814
<hr/>		<hr/>		<hr/>	
16.85228		12.12906		(111.8050)	

The mean of all three series gives  $Cd=111.8015$ , when  $O=16$ .

Partridge does not state what atomic weights he assumes for C and S, but recalculation shows that he must have taken the even numbers 12 and 32. With Stas' values, the results are much less concordant.—*Am. Jour. Sci.*, Nov., 1890.

**Nickel.**—Mond, Langer, and Quincke, in their paper upon nickel-carbon oxide,  $NiC_2O_4$ , have prepared pure nickel from that compound and converted it into  $NiO$ . The latter, reduced in  $H$ , gave the following results, when  $O=16$ :

0.2414	gm. $NiO$ gave	0.1896	Ni	Ni =	58.58
.3186	"	.2503	"	"	58.64
.3391	"	.2663	"	"	58.52

—*Jour. Chem. Soc.* 57, 753.

## ORGANIC ANALYSIS.

**A Morphiometric Assay of Opium.**—The Analyst, **16**, 198; also, Am. Journ. Pharm.

5 gms. of the finely powdered opium are triturated with water and made up to 78 gms. After frequent agitation during two hours, 60.8 gms. (=4 gms. opium) are filtered off, and 0.2 gm. oxalic acid added to the filtrate. After standing half an hour, 5.2 gms. of potassium carbonate solution (1 : 2) are added, and the solutions are thoroughly mixed. 16.5 gms. are filtered at once through folded filter into a tared flask of 30 cc. capacity. To this filtrate (=1 gm. opium) are added 5 gms. ether free from alcohol, and the corked flask is shaken violently for ten minutes. The ether is then evaporated by means of a jet of air, the morphia collected on a filter, and thorough washed with water saturated with ether. The precipitate is dried at 50° C., returned to the dried flask, and weighed until the weight is constant. For *extract of opium*, 2.5 gms. are taken, dissolved in water with 0.2 gm. oxalic acid and diluted to 70 gms. 5 gms. potassium carbonate solution are added and 15 gms. (=0.5 gm. extract) of the mixture are filtered off.

For *tincture of opium*, 50 gms. are taken with 0.2 gm. oxalic acid and evaporated to a thin extract. This is gradually diluted with water to 70 gms. To it are added 5 gms. potassium carbonate solution, and 15 gms. (=10 gms. tincture) are filtered off. This method gives results that are about 1 per cent. lower than those obtained by Dieterich's method, and duplicates are not more than 0.3 per cent. apart. s. c.

**Detection of Nitrobenzene in Oil of Bitter Almonds and Soaps.**—J. Morpurgo, Pharm. Post., The Analyst **16**, 198.

The suspected oil is warmed with manganese dioxide and sulphuric acid. Nitrobenzene does not lose its odor by this treatment, but on the contrary becomes more pronounced, and after standing, the odor of oil of cinnamon is developed. Oil of bitter almonds at first develops a disagreeable odor, which, after some time, disappears entirely.

Soaps are dissolved in water, the solution treated with an excess of slaked lime, and extracted with ether. The ethereal solution is evaporated to dryness on a water bath, and the residue

shaken up with a little water. In a small porcelain dish are placed 2 drops of carbolic acid (10 parts water + 100 parts crystallized acid), 3 drops distilled water, and a piece of caustic potash the size of a pea. The mixture is carefully heated to boiling, and a few drops of the ethereal residue solution added. On continued boiling, a carmine-red ring around the edge of the liquid will show the presence of nitrobenzene. The addition of calcium hypochlorite solution changed the red to a beautiful green. S. C.

**Characteristic Reaction of Cocain.**—(C. R. 111, 348; M. Ferrira da Silva).

A small quantity of cocain, or one of its salts, is treated with a few drops of fuming nitric acid (1.4); evaporated to dryness, and the residue treated with 1 or 2 drops of a concentrated alcoholic solution of potash, thoroughly mixing with a glass rod. A peculiar odor is noticed which resembles powdered mint. This is nearly the proceeding for the color reaction for atropin (method of Vitali) but has been used heretofore only for color reactions.

This reaction permits of the differentiation of cocain from other alkaloids of the same group. Cocain belongs to that class of alkaloids which can be taken up from ammoniacal solutions by benzine. The other members of the group are:

- |               |                 |
|---------------|-----------------|
| 1. Atropin.   | 8. Narcotin.    |
| 2. Brucin.    | 9. Pilocarpin.  |
| 3. Cinchonin. | 10. Quinin.     |
| 4. Codein.    | 11. Quinidin.   |
| 5. Delphinin. | 12. Sabidillin. |
| 6. Eserin.    | 13. Strychnin.  |
| 7. Hyoscamin. | 14. Veratrin.   |

Of the above, 1, 7, 13, 4 and 6 give colorations, and 6 also a disagreeable odor resembling phenylcarbylamin; 5, 2 and 14 give a less active odor, which cannot be confounded with that produced from cocain. The other alkaloids do not give sensible reactions.

The reaction for cocain is not only characteristic, but also very sensitive. Half a milligram of cocain chlorhydrate can be detected.

H. W. W.

**Furfurol in Spirits.**—L. Lindet, C. r. 111, 236.

The presence of furfurol in spirits is revealed by the color reaction which it gives with the acetate of anilin. This reaction may also be used quantitatively.

It was found that in spirits distilled over the naked fire or from fermentation, where the grains had been previously treated with acids, furfural was always present. In other alcoholic products it was absent. A sample of brandy was found to contain .2 cc. furfural per liter. Brandies from grape marcs were found to contain as high as .4 cc per liter.

The furfural is believed to come from the torrefaction to which the organic matter in contact with the bottom of the vessel is subjected when heated over the naked fire, and from the action of the acids on the envelopes of the seeds in the case where acids have been fused. Furfural is therefore not to be regarded as a normal product of fermentation, as is the case with glycerine, acetic and succinic acids, etc.

H. W. W.

**Estimation of Ash in Sugars by Incineration with Benzoic Acid.**—C. r. 111, 190.

To avoid the correction of one-tenth, as proposed by Scheibler, and one-fifth, as proposed by Girard and Violette, when sugars are burned with  $\text{H}_2\text{SO}_4$ , Boyer suggests incineration with benzoic acid, as giving the real quantity of mineral matter without correction.

The benzoic acid is dissolved in alcohol of 90 per cent. 25 gms. of the acid to 100 cc. of alcohol. 5 gms. of the sugar are weighed in a capsule and moistened with 1 cc.  $\text{H}_2\text{O}$ . The capsule is heated slowly in order to caramelize the sugar without carbonizing it. 2 cc. of the benzoic acid are next added, and the capsule warmed until all the alcohol is evaporated. The temperature is then elevated until the sugar is converted into carbon. The decomposing benzoic acid produces abundant vapors, which renders the mass extremely porous, especially if a circular motion is imparted to the capsule. The slow heating is continued until all the benzoic acid is volatilized. The carbon obtained is voluminous and of a brilliant black color. The incineration is accomplished in a muffle at a low red heat. The capsule should be weighed quickly when taken from the desiccator, in order to avoid the absorption of water by the alkaline carbonates.

Benzoate of ammonia may be employed instead of benzoic acid, and the analyst should previously assure himself that neither the acid nor the ammonia salt leaves a residue on incineration.

In addition to giving the mineral matters directly, this method permits the determination of their composition also—a matter of no small importance.

H. W. W.

## NEW BOOKS.

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The preliminary report of the committee may be found in the *JOURNAL OF ANALYTICAL CHEMISTRY*, Vol. 3, p. 398, and it is with a view of placing before the students of this institution analytical methods based upon such report that these notes have been prepared." From this statement the character of the contents may be inferred. 12 mo., 48 pp.

**Spencer's Handbook for "Sugar Manufacturers."‡**—This

\**Lessons in Chemical Philosophy.* By John Howard Appleton, Professor of Chemistry in Brown University. Second Edition; 256 pp. Silver Burdett & Co., New York—Boston—Chicago. 1890. Price, \$1.40.

†*Examination of Potable Water.* By W. P. Mason, Professor of Analytical Chemistry, Rensselaer Polytechnic Institute. Troy, N. Y. Mins & Knight, 1890.

‡*A Handbook for Sugar Manufacturers and their Chemists. Containing Practical Instruction in Sugar House Control, the Diffusion Process, Selected Methods of Analysis, Reference Tables, etc., etc.* By Guilford L. Spencer, A. C., of the U. S. Department of Agriculture. New York: John Wiley & Sons. \$2.00.

little book is evidently the result of practical experience in sugar house work of a good analytical chemist. It is written by a man who knows what is and what is not needed, and is sure to be of value to sugar house chemists. It is gotten up in pocket diary form (pages  $4 \times 6\frac{1}{2}$  inches), and contains a full set of blank pages for the record of daily practice.

**Wiechman's Sugar Analysis.\***—This book may be regarded as a companion volume to the preceding. It is written from the standpoint of one making analyses of the completed product. The book is perhaps better adapted for a text-book than Spencer's work already mentioned above.

**Smith's Electro-Chemical Analysis.†**—This is one of the small monographs intended for students' use. Many points are not treated so fully as might be desired by the experienced analyst, but this could scarcely be expected in a work of the size. In all cases the author has given a bibliography of the subjects treated, so that the book is of value to the older as well as to the younger student. Dr. Smith has given a great deal of study to this branch of chemical analysis, and, as might have been expected, he has produced a thoroughly good book. It is to be hoped that he may be able at some future time to prepare a larger and somewhat fuller treatise.

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## NOTES.

**Obituary.**—Silas H. Douglas died in Ann Arbor, Mich., August 23, 1890, at the age of seventy-four years. He has been professor of chemistry in the University of Michigan from 1848 to 1877. The Chemical laboratory of this institution, erected in 1856, and repeatedly extended, was the product of his labors, continued with energy through the active portion of his life. For a number of years his health has been infirm, and he has remained in the retirement of his devoted family.

A. B. P.

\***Sugar Analysis.** For Refiners, Sugar Houses, Experimental Stations, etc., and as a Handbook of Instruction in Schools of Chemical Technology. By Ferdinand G. Wiechmann, Ph. D., Instructor in Chemical Physics and Chemical Philosophy, School of Mines, Columbia College, Consulting Chemist to the Havemeyers and Elder Sugar Refining Company, Brooklyn, N. Y. New York: John Wiley & Sons, 1890.

†**Electro-Chemical Analysis.** By Edgar F. Smith, Professor of Analytical Chemistry, University of Pennsylvania, with 25 illustrations. 12mo. 116 pp. \$1.00, Philadelphia, P. Blakiston, Son & Co., 1890.

# Index to Vol. IV, 1890.

	PAGE.
ACIDIMETRY, Standardization of Solutions for . . . . .	424
Acids, Volumetric Determination of . . . . .	218
<i>A Gravimetric Method for Obtaining a Constant Ratio of Reduction of Copper with Reducing Sugars.</i> By J. L. Fueling . . . . .	386
Aignan, A. On a Sophistication of Linseed Oil . . . . .	345
Air, Determination of Oxygen in . . . . .	457
Albumen in Urine, Determination of . . . . .	109, 114
Alcohol, Purification of, 86; Method for Titrating with Chromic Acid . . . . .	96
Aliquotimeter . . . . .	178
Alizarin Oil, Estimation of Fatty Acids in . . . . .	101, 237
Alkalies in Presence of Sulphates, Determination of . . . . .	324
Alkalies, Occurrence of Boracic Acid as an Impurity in Caustic . . . . .	197
Alkalimetry, Standardization of Solutions for . . . . .	424
Alloys of Copper and Zinc, Analysis of . . . . .	210
Alt, H. Standardization of Silver Solution, 55; Gravimetric Determination of Thiocyanates . . . . .	103
Alumina and Iron Oxide, Precipitation of by Ammonia, 81; in Phosphates, Estimation of . . . . .	69, 214
Aluminum, Analysis of Metallic . . . . .	228
Aluminum and Manganese, Separation from Iron by Means of Nitroso-Beta-Naphthol . . . . .	335
Aluminum in Iron and Steel Determination, 337; Determination of Minute Quantities in . . . . .	225
<i>A Method for the Determination of Iodine in Haloid Salts.</i> By F. A. Gooch and P. E. Browning . . . . .	124
<i>A Method for the Reduction of Arsenic Acid in Analysis.</i> By F. A. Gooch and P. E. Browning . . . . .	282
<i>A Modified Method of Executing the Potassium Ferrocyanide Test in Glucose Determinations.</i> By B. B. Ross . . . . .	427
Ammonia, Estimation by Ruffie's Method, 326; Effect of Temperature on Nesslerization of . . . . .	454
Ammonia Free Water . . . . .	71
Ammonia Solution, The Use of Normal . . . . .	204
A Modified Form of Pinch-cock . . . . .	34
Andrews, L. W. Volumetric Estimation of Combined Sulphuric Acid . . . . .	73
<i>A New Form of Hydrometer.</i> By G. H. Failyer . . . . .	308
<i>A New Method for Standardizing the Solutions used in Alkalimetry and Acidimetry.</i> By Edward Hart and Stuart Croasdale . . . . .	424
<i>A New Method for the Estimation of Theine in Teas.</i> By G. L. Spencer . . . . .	158
<i>A New Process for the Sure Detection of Sugar in Urine.</i> By H. A. Bishop . . . . .	139
A New Test-tube Holder. By J. T. Stoddard . . . . .	34
<i>A New Valve for Wash-Bottles.</i> By David H. Browne . . . . .	141
<i>An Examination of Fusel Oil.</i> By J. H. Long and C. E. Linebarger . . . . .	29
<i>An Improved Coil for Milk Analysis.</i> By Charles Rice, New York . . . . .	155
<i>An Improved Method for the Estimation of Theine in Tea.</i> By G. L. Spencer . . . . .	390
Apparatus for Determining Nitrogen by the Method of Kjeldahl . . . . .	179
Apparatus for Determining Nitric Acid . . . . .	188
Apparatus for Drying in Hydrogen . . . . .	175
Arsenic Acid, Method for Reduction of, 282; Rapid Estimation of . . . . .	320
Arsenic, in Bone-Meal, Determination of, 74; Separation from Copper by Electrolysis . . . . .	459
Arth, G. The Determination of Phosphoric Acid in Basic Slags . . . . .	459
Ash Determination . . . . .	97
Ash in Sugars, Determination of . . . . .	102, 103, 467
Aslanoglon, P. L. Electrolysis of Different Substances . . . . .	460
Atomic Weights, of Oxygen, 106; Palladium, 106; Gold, 106; Magnesium, 333; Lanthanum, 333; Indium, 334; Bismuth, 334; Proper Standard for, 365; Fluorine, 461; Oxygen, 461; Glucium, 462; Manganese, 463; Cadmium, 463; Terbium and Gadolinium . . . . .	463

	PAGE.
BACTERIA, Poisonous Products of . . . . .	358
Baginsky and Startthagen. Poisonous Products of Sapogenous Intestinal Bacteria . . . . .	358
Bailey, G. H. Determination of Sulphur in Coal . . . . .	83
Baihache. Determination of Nitrogen in Nitrates . . . . .	211
Baking Powder, Analysis of . . . . .	231
Ballantyne, H. See Thomson, R. T.	
Barium, Strontium, and Calcium, Separation of . . . . .	76
Barth, K. See Hefelmann, R.	
Basic Slags, Determination of Phosphoric Acid in . . . . .	459
Bauman, A. Preparation of Oxygen from Peroxide of Hydrogen, 202; Analysis of Pyrolusite . . . . .	216
Beam, W. See Leffman, H.	
Bein, Dr. Determination of Igniting Point of Explosives . . . . .	57
Bell, J. C. Determination of Iron in Water . . . . .	82
Benedikt, R., and A. Grüssner. Quantitative Determination of the Methoxy Group . . . . .	94
Benzene in Illuminating Gas, Determination of . . . . .	231
Berthelot, M. Graduation of Tubes for Gasometric Apparatus, 202; Estimation of Benzene in Illuminating Gas . . . . .	231
<i>Bibliography of Analytical Chemistry for the Year 1889.</i> By H. Carrington Bolton . . . . .	48
BISHOP, H. A. Detection of Sugar in Urine . . . . .	139
Bishop, M. W. Detection of Oil of Sesame in Olive Oil . . . . .	92
Bismuth, Atomic Weight of . . . . .	334
Blast Furnaces, Titanium in . . . . .	227
Blochmann, R. The Concentration of Reagents . . . . .	199
Blood, Determination of the Alkalinity of the . . . . .	115
Blowpipe Test for Mercury . . . . .	461
Bloxam, A. G. Ammonia Free Water . . . . .	71
Boam, F. A Simple Gas Generator, 310; The Rapid Estimation of Arsenic . . . . .	320
Bocklary, Estimation of Cotton-seed Oil in Lard . . . . .	350
Boiler Scale, The Composition of . . . . .	24
Boisbaudran. Atomic Weights of Gadolinium and Terbium . . . . .	463
BOLTON, H. CARRINGTON. Bibliography of Analytical Chemistry for 1889 . . . . .	48
Bone Meal, Determination of Arsenic in . . . . .	74
Boric Acid, Determination of in Wine, 102; Distribution of in Plants, 191; in Caustic Alkalies as an Impurity . . . . .	197
Borman, K. The Götz Method for Determining Phosphorus in Steel . . . . .	83
Bourcart, R. Method for Titrating Alcohol with Chromic Acid . . . . .	96
Boyer. Estimation of Ash in Sugars by Incineration with Benzoic Acid . . . . .	467
Brieger and Frühkel. The Chemical Poison of Diptheria . . . . .	358
Breneman, A. A. The Alleged Sterilization of River Water by Mine Water . . . . .	207
Bromine, Volumetric Estimation of in Presence of Chlorine and Iodine, 69; Determi- nation of in Presence of Chlorine, 167; Decomposition of Sulphides with . . . . .	221
BROWNE, DAVID H. Valve for Wash-Bottles . . . . .	141
BROWNING, P. E. See Gooch, F. A.	
Brugnatelli, E. Detection of Mercury in Urine . . . . .	91
Brulle, R. Reactions of Silver Nitrate on Vegetable Oils . . . . .	239
Buchan, A. Estimation of Ammonia by Ruffie's Method . . . . .	326
Buisine, A. and P. Note on Pretended Reagent for Copper . . . . .	217
Burghardt, C. A. On Some Applications of Caustic Soda or Potash and Carbon in the Analysis of Minerals . . . . .	322
Burton, W. M. Rapid Estimation of Sulphur in Organic Compounds . . . . .	90
Burton and Voree. Atomic Weight of Magnesium . . . . .	333
CALCIUM, Barium, and Strontium, Separation of . . . . .	76
Calcium Chloride Tube, A Substitute for in Ultimate Analysis . . . . .	58
Cadmium, Determination as Sulphide, 332; in Cadmium Dust, Determination of, 80; in Zinc Refuse, Determination of, 213; Atomic Weight of . . . . .	463
Cane Sugar, Determination of in Liquors, Confectionery and Chocolate . . . . .	98
CALLISON, J. S. Boracic Acid in Plants, 191. See also Venable, F. P.	



	PAGE.
Carbon, Determination in Iron and Steel, 403; and Sulphur, Simultaneous Estimation of, in Organic Substances . . . . .	105
Carbon Dioxide, Estimation of Dissolved, 77; Apparatus for the Direct Determination of, 204; Estimation in Drinking Water Containing Magnesia, 217; Free and Combined in Water . . . . .	457
CATLIN, CHARLES A. Commercial Valuation of Cream of Tartar Substitutes . . . . .	361
Cazeneuve, P., and L. Hugounenq. Determination of Nitrogen, 77; Determination of Nitrogen in Urine . . . . .	109
Cellulose, Quantitative Determination of . . . . .	95
Centrifugal Action in Laboratory Work . . . . .	198
Chamberland. See Roux.	
Charlton, T. Blowpipe Test for Mercury . . . . .	461
Chemical Reagents, System of, Based on the Equivalents . . . . .	317
Chili Saltpeter, Estimation of Nitrogen in . . . . .	456
Chlorine and Iodine, Volumetric Estimation of Bromine in Presence of, 69; Determination in Water, 82; Determination of Bromine in Presence of, 167; Detection and Determination in Sulphocyanide of Potash, 223; Determination when Mixed with Iodine, 243; Determination when Mixed with Hydrochloric Acid . . . . .	328
Chlorine Water, Decomposition of by Light . . . . .	66
Chocolate, Determination of Cane Sugar in, 98; Analysis of . . . . .	338
Chromic Acid, Method for Titrating Alcohol with . . . . .	96
Chromic Chloride, Method of Preparing . . . . .	59
Chromium Steel, Analysis of . . . . .	227
Clark, Harry W. See Hazen, Allen.	
Classes. Atomic Weight of Bismuth . . . . .	334
Coal, Determination of Sulphur in . . . . .	83
Cocain, Characteristic Reaction of . . . . .	466
Cocoa-Butter, Iodine Number of . . . . .	345
Cohen, J. B. Wiborgh's Method for the Analysis of Sulphur in Iron and Steel, 335. See also Grant, Jas., and Oddy, R. W.	
Coil for Milk Analysis, An Improved . . . . .	155
Colorimetric Determination of Nitric Acid . . . . .	209
Colorimetric Methods for the Determination of Nitrates in Potable Waters . . . . .	67, 208
Combustible Gases, Detection of, in the Atmosphere . . . . .	313
<i>Commercial Valuation of Cream of Tartar Substitutes.</i> By Charles A. Catlin . . . . .	361
Committee on Methods of Sugar Analysis of the Louisiana Sugar Chemists' Association, Report of the . . . . .	1
<i>Conversion of "Parts per Million" into "Grains per Gallon."</i> By Wm. P. Mason . . . . .	121
Confectionery, Determination of Cane Sugar in . . . . .	98
Copper, Pretended Reagent for, 217; Volumetric Determination of, 210, 212, 319, 320; Test for in Glucose Determinations, 427; Separation from Arsenic by Electrolysis, 459	
Copper and Zinc Alloys, Analysis of . . . . .	210
Cotton-Seed Oil in Lard, Test for, 238; Estimation of . . . . .	350
Crafts, J. M. Purification of Mercury . . . . .	59
Craig, G. Analysis of Silicates . . . . .	63
Crampton, C. A. Analysis of Baking Powder . . . . .	231
Cream, Determination of Fat in . . . . .	102
Cream of Tartar Substitutes, Valuation of . . . . .	361
CROASDALE, STUART. See Hart, Edward.	
Crude Fiber, Determination of . . . . .	35
DANCY, F. B. On the Determination of Available Phosphoric Acid in Fertilizers Containing Cotton-Seed Meal . . . . .	395
DeKoninck, L. L. The Use of Nitroso-Beta Naphthol for the Determination of Iron and for its Separation from Manganese and Aluminum . . . . .	335
<i>Detection and Quantitative Estimation of Inorganic and Organic Poisons in Bodies.</i> By Dr. Anton Seyda . . . . .	288
<i>Determination of "Total Residue" in Water Analysis.</i> By W. P. Mason . . . . .	53
Dextrose, Determination of . . . . .	253
Diphtheria, Chemical Poison of . . . . .	358

	PAGE.
Donath, E. Estimation and Separation of Tellurium, 319; and G. Hattensaur. Volumetric Determination of Zinc and Copper . . . . .	212
Douglas, Silas H. Obituary Notice . . . . .	480
DROWN, THOMAS M. The Filtration of Natural Waters . . . . .	428
Drying in Hydrogen, Apparatus for . . . . .	175
Drying Oven for Forage Samples . . . . .	184
EASTERFIELD, T. H. Water Bath Regulator . . . . .	56
EDSON, HUBERT. Preservation and Analysis of Sugar Solutions . . . . .	381
EHRENFELD, C. H. Stilbite from York Co., Pa., 157; Fluorite from York, Pa. . . . .	281
Electricity in Chemical Manipulations . . . . .	312
Electrolysis, Separation of Copper from Arsenic by, 459; of Different Substances . . . . .	460
Electrolytic Determination of Metals, Apparatus for . . . . .	57
Ernest, S. Electro-Deposition of Silver . . . . .	460
Essential Oils, Estimation of by Maumene's Test . . . . .	237
Etard, A., and P. Lebeau. Volumetric Determination of Copper . . . . .	210
Excelsior Springs, The Manganese Waters of . . . . .	208
Explosives, Determination of Igniting Point of . . . . .	57
Extraction Apparatus . . . . .	314
FAILYER, G. H. A New Form of Hydrometer . . . . .	308
Fats, Estimation of in Milk, 89, 102; Detection of Cotton-Seed Oil in, 90; Determination of in Linseed Oil Cake, 97; Comparative Results in the Analysis of, 104; Extraction from Milk Solids, 279; and Oils, Revision of Constants Employed in the Analysis of . . . . .	347
Fatty Acids in Alizarin Oil, Estimation of . . . . .	101, 237
Fatty Bodies in Vegetable Organisms, Estimation of . . . . .	392
Fehling's Solution, Conversion Table for . . . . .	329
Ferments, Peptic and Diastatic . . . . .	353
Fermi, Dr. Claudio. The Peptic and Diastatic Ferments of Micro-Organisms . . . . .	353
Ferric Salts, Preparation of a Standard Solution of Without Titration . . . . .	67
Ferrira da Silva. Characteristic Reaction of Cocain . . . . .	466
Ferro-Chromium, Analysis of . . . . .	227
Ferro-Tungsten, Analysis of . . . . .	227
Fertilizers, Determination of Nitrates in . . . . .	455
Fessenden, R. A. Electricity in Chemical Manipulations, 312; Volumetric Analysis of Copper . . . . .	319, 320
Filsinger, F. Analysis of Chocolate, 338; Iodine Number of Cocoa-Butter . . . . .	345
Filtering Arrangement . . . . .	311
Filter, Simple Form of Quick . . . . .	315
Filtration of Natural Waters . . . . .	428
Filtration under Pressure . . . . .	34
Flückiger, F. A. Ash Determination . . . . .	97
Fluorine, Atomic Weight of . . . . .	461
Fluorite from York, Pa. By C. H. Ehrenfeld . . . . .	281
Hoerster, O. Determination of Nitrogen in Nitric Acid by Kjeldahl's Method, 224; Estimation of Nitrogen in Chili Saltpeter . . . . .	456
Forage Samples, Drying Oven for . . . . .	184
Fredheim, C. Separation of Vanadic and Tungstic Acids . . . . .	222
French, W. Preparation of a Standard Solution of Ferric Salts without Titration . . . . .	67
Fresenius, H. Determination of Arsenic in Bone Meal . . . . .	74
Fresenius, W. Examination of and Determination of Phosphoric Acid in Wines . . . . .	86
Frühkel. See Brieger.	
FUELING, J. L. A Gravimetric Method for Obtaining a Constant Ratio of Reduction of Copper with Reducing Sugars . . . . .	386
Furfural in Spirits . . . . .	466
Fusel Oil, an Examination of . . . . .	29
Fusion Mixture for Analysis of Minerals . . . . .	322

	PAGE.
<i>GADOLINITE from Llano County, Texas.</i> By E. Goldsmith . . . . .	22
Gadolinium and Terbium, Atomic Weight of . . . . .	463
Gallic and Tannic Acids, Bottinger's New Reaction for . . . . .	341
Gantter, F. Estimation of Tannin by Permanganate of Potash . . . . .	93
Gas Analysis, Contributions to . . . . .	58
Gas Burner for Laboratory Use . . . . .	57
Gas Desiccator . . . . .	172
Gases, Detection of Combustible . . . . .	313
Gas, Estimation of Benzene in Illuminating . . . . .	231
Gas Generator . . . . .	310
Gasometric Apparatus, Graduation of Tubes for . . . . .	202
Gastric Juice, Determination of Free Hydrochloric Acid in . . . . .	115
Generator for Sulphuretted Hydrogen . . . . .	205
Genieser, A. Determination of the Specific Gravity of Sirups . . . . .	202
GILBERT, JAMES P. Determination of Silica in Silicates by Fusion with Alkaline Carbonates . . . . .	159
Glaser, E. Estimation of Alumina and Oxide of Iron in Phosphates . . . . .	69
Glucinum, Atomic Weight of . . . . .	462
Glycerine, Estimation of Commercial, 96; Estimation in Soap Lyes and Crude Glycerine . . . . .	343
Glucose Determinations, Test for Copper in . . . . .	427
GOLDSMITH, E. Gadolinite from Texas . . . . .	22
Götz Method for Determining Phosphorus in Steel . . . . .	83
GOOCH, F. A., and P. E. Browning. Determination of Iodine in Haloid Salts, 124; A Method for the Reduction of Arsenic Acid in Analysis, 282; and F. W. Mar, Two Methods for the Direct Determination of Chlorine in Mixtures of Alkaline Chlorides and Iodides . . . . .	243
Gore, Dr. G. Decomposition of Chlorine Water by Light, 66; Test for Impurities in Mercury . . . . .	80
Graduation of Tubes for Gasometric Apparatus . . . . .	202
"Grains per Gallon," Conversion of "Parts per Million" to . . . . .	121
Grant, Jas., and J. B. Cohen. Determination of Alkalies in Presence of Sulphates . . . . .	324
Griffiths, A. B. A Ptomaine Extracted from Urine in a Case of "Mumps" . . . . .	351
Grittner, A. Estimation of Zinc and Nitrogen in Impregnated Railroad Ties . . . . .	457
Grober, J. V. Determination of Ash in Sugars . . . . .	102
Gröger, M. A New Gas Burner . . . . .	57
Grüssner, A. See Benedikt, R.	
Gueney, E. Volumetric Determination of Tannin . . . . .	342
Guthrie, F. Estimation of Fatty Acids in Alizarin Oil . . . . .	101
Gyzander, C. R. Filtering Arrangement . . . . .	311
HALL, CHARLES C. Rapid Determination of Bromine in Presence of Chlorine . . . . .	167
Hall, C. M. See Hunt, A. E.	
Halogens, Errors in the Determination of Nitrogen in Bodies Containing the, 88; Determination of Free . . . . .	321
Haloid Salts, Determination of Iodine in . . . . .	124
Haltensaur, G. See Donath, E.	
Hamilton, R. Purification of Hydrofluoric Acid . . . . .	56
Harpe, C. de la. See Reverdin, F.	
HART, EDWARD, and STUART CROASDALE. A New Method for Standardizing the Solutions, used in Alkalimetry and Acidimetry . . . . .	424
Haycraft, J. B., and Williamson, R. J. Determination of the Alkalinity of the Blood . . . . .	115
Hazen, A. Determination of Chlorine in Water, 82; and Harry W. Clark, Effect of Temperature upon the Determination of Ammonia by Nesslerization . . . . .	454
Heating Crucibles, Oven for . . . . .	59
Hefelmann, R., and K. Barth. Determination of Oxygen in Water by Müller's Method . . . . .	78
Hehner, O. The Estimation of Glycerine in Soap Lyes and Crude Glycerine . . . . .	343
Hempel, W. Determination of Phosphorus in Phosphor-Tin . . . . .	83
Hinsdale, S. J. Colorimetric Method for Estimating Tannin in Barks, etc. . . . .	341
Höbling, V. A New Titration Apparatus . . . . .	198

	PAGE.
HORTON, H. E. L. Some Notes on the Determination of Sugars with Fehling's Solution	370
Hugouneng. See Cazeneuve, P.	
Humus in Soils, Determination of . . . . .	322
Hundeshagen, F. Analytical Studies on Phosphododekamolybdic Acid . . . . .	60
Hunt, A. E., J. W. Langley, and C. M. Hall. Analysis of Metallic Aluminum . . . . .	228
Hydrochloric Acid, Determination of Free in Gastric Juice, 115; Estimation of Free in Stannous Chloride, 216; Determination of when Mixed with Chlorine . . . . .	328
Hydrofluoric Acid, Pipette for, 48; Purification of . . . . .	56
Hydrogen, Apparatus for Drying in . . . . .	175
Hydrogen Generator . . . . .	169
Hydrometer, New Form of . . . . .	308
<i>ILLUSTRATIONS of Sewage Decomposition in Streams.</i> By J. H. Long . . . . .	39
Improved Soxhlet Extractor and Apparatus for Distilling in a Vacuum . . . . .	55
Impurity in Chemicals of U. S. Pharmacopoeia . . . . .	316
Indicator (Alpha Naphthol-Benzoin) a New . . . . .	315
Indigotine, Determination of . . . . .	103
Indium, Atomic Weight of . . . . .	334
<i>International Standards for the Analysis of Iron and Steel.</i> By John W. Langley . . . . .	403
Iodides in Presence of Chlorine and Bromine, Determination of . . . . .	321
Iodine, Determination in Haloid Salts, 124; Determination of When Mixed, with Chlorine . . . . .	243
Iodine and Chlorine, Volumetric Estimation of Bromine in Presence of . . . . .	69
Iron, Determination in Water, 82; Separation from Manganese and Aluminum by Means of Nitroso-Beta-Naphthol, 335; Determination of Aluminum in . . . . .	337
Iron and Steel, Determination of Minute Quantities of Aluminum in, 225; Sulphur in, 335; Carbon in . . . . .	403
Iron Ore, Phosphorus in . . . . .	268
Iron Oxide and Alumina, Precipitation of by Ammonia, 81; in Phosphates, Estimation of . . . . .	69, 214
Iron Oxide in Phosphates . . . . .	215
Isbert and Venator. Examination of Milk . . . . .	231
JANNASCH, P. Analysis of Pyrites, 220; Decomposition of Sulphides with Bromine Vapor, 221; of Pyrites in a Current of Oxygen . . . . .	222
Jelowitz, E. Determination of Free and Combined Carbonic Acid in Air . . . . .	457
Johnson, A. E. Colorimetric Determination of Nitrates in Potable Waters . . . . .	208
JOHNSON, S. W. Laboratory Apparatus . . . . .	169
Johnstone, A. Detection of Tin in Minerals . . . . .	66
Jolles, A. Determination of Free Tartaric Acid in Vinegar . . . . .	102
Jolly. Atomic Weight of Indium . . . . .	334
JONES, CLEMENS. Phosphorus in Pig-Iron, Steel and Iron Ore . . . . .	268
Jones, R. Determination of Iron and Aluminum Oxides in Phosphates . . . . .	214
Jüptner, H. von. Oven for Heating Crucibles . . . . .	59
KIBBLE, W. O. Sulphuretted Hydrogen Generator . . . . .	205
Kipp's Apparatus, a Substitute for, 54; for Preparing Oxygen . . . . .	202
Kissling, R. An Investigation of Sodium Carbonate . . . . .	202
Klingemann, F. Amount of Nitrous Oxide Found in the Combustion of Organic Substances . . . . .	97
Klopsch, R. Determination of Fat in Linseed Oil Cake . . . . .	97
Knöfler, Dr. O. New Extraction Apparatus . . . . .	314
Krüss & Moraht, Atomic Weight of Glucinum . . . . .	462
König, J. Methods of Stating the Analysis of Wines . . . . .	93
Kupferschlaeger, Prof. Separation of Barium, Strontium, and Calcium . . . . .	76
LANGE, G. Quantitative Determination of Cellulose . . . . .	95
Langer. See Mond.	
LANGLEY, JOHN W. International Standards for the Analysis of Iron and Steel . . . . .	403
Langley, J. W. See Hunt, A. E.	

	PAGE.
Lanthanum, Atomic Weight of . . . . .	333
Lard, Testing for Beef Stearin in, 89; Test for Cotton-seed Oil in, 238; Estimation of Cotton-seed Oil in . . . . .	350
Lead Poisoning by Carbonated Beverages . . . . .	353
Lebeau, P. Volumetric Determination of Free Halogens and the Determination of Iodides in Presence of Chlorine and Bromine . . . . .	321
Lebeau, P. See Etard, A.	
Leffman, H., and W. Beam. Centrifugal Action in Laboratory Work . . . . .	198
Leone, T. Detection of Cotton Oil in Fats and Olive Oil . . . . .	90
Levoir, L. C. Apparatus for the Electrolytic Determination of Metals . . . . .	57
Levulose, Determination of . . . . .	253
Lewkowitsch, J. Improved Soxhlet Extractor and Apparatus for Distilling in a Vacuum . . . . .	55
Lindet, L. The Simultaneous Estimation of Saccharose and Raffinose in Commercial Products . . . . .	349
Lindet, L. Furfural in Spirits . . . . .	466
LINEBARGER, C. E. See J. H. LONG.	
Lignon, M. Lee Linossier, G.	
Linossier, G., and M. Lignon. Volumetric Determination of Acids . . . . .	218
Linseed Oil, a Sophistication of . . . . .	345
Linseed Oil Cake, Determination of Fat in . . . . .	97
Liquers, Confectionery and Chocolate, Determination of Cane Sugar in . . . . .	98
LONG, J. H., AND C. E. LINEBARGER. An Examination of Fusel Oil . . . . .	29
LONG, J. H. Sewage Decomposition in Streams . . . . .	39
Louisiana Sugar Chemists' Association, Report of the Committee on Methods of Sugar Analysis . . . . .	I
Lunge G. Detection of Nitrous Acid, 81; Precipitation of Alumina and Iron-Oxide by Ammonia . . . . .	81
Lunt, Joseph, and H. E. Roscoe. Schützenberger's Process for the Estimation of Dissolved Oxygen in Water . . . . .	71
MCCAY, LEROY W. Separation of Copper from Arsenic by Electrolysis . . . . .	459
McCullough, N. Volumetric Estimation of Bromine in Presence of Chlorine and Iodine . . . . .	69
Magnesium, as a Reagent, 54; Atomic Weight of . . . . .	333
Mallet, J. W. Atomic Weight of Gold . . . . .	106
Malt, Estimation of Available Extract in . . . . .	92
Manganese, Separation from Zinc, 69; Determination in Slags and Ores, 267; and Aluminum, Separation from Iron by Means of Nitroso-Beta-Naphthol, 335; Atomic Weight of . . . . .	463
Manganese Waters of Excelsior Springs . . . . .	208
Manipulation, A Brief Summary of Practical . . . . .	203
Mann, C. Determination of Chlorine in Sulphocyanide of Potash . . . . .	223
MAR, F. W. See Gooch, F. A.	
MASON, W. P. Determination of "Total Residue" in Water Analysis, 53; Conversion of "Parts per Million" to "Grains per Gallon," 121; The Manganese Waters of Excelsior Springs . . . . .	208
Maumene's Test for Essential Oils . . . . .	237
MAXWELL, WALTER. On the Methods of Estimation of the Fatty Bodies in Vegetable Organisms . . . . .	392
Mayer's Reagent, Behavior of Quinine Alkaloids towards . . . . .	104
Meat, Analysis of Tinned . . . . .	338
Meat Extracts, Method for Examination of . . . . .	105
Method for the Rapid Determination of Manganese in Slags, Ores, etc. By Fred. G. Myhlertz . . . . .	267
Methoxy Group, Quantitative Determination of . . . . .	94
Mercury, the Purification of, 59; Test for Impurities in, 80; Detection in Organic Bodies and Urine, 91; Blowpipe Test for . . . . .	461
Milk, Rapid Estimation of Fat in, 89; Determination of Fat in, 102; Examination of . . . . .	231
Milk Analysis, 337; An Improved Coil for . . . . .	155
Milk Analysis. By H. Droop Richmond . . . . .	26, 241
Milk Solids, Extraction of Fat from . . . . .	279
Minerals, Use of Caustic Soda or Potash and Carbon in Analysis of . . . . .	322
Mineral Waters, Determination of Lithia in . . . . .	325

	PAGE.
Minor, W. The Use of Oxygen in Quantitative Analysis, 57; Determination of Cadmium in Cadmium Dust, 80; Determination of Cadmium in Zinc Refuse, 213; Estimation of Free Hydrochloric Acid in Stannous Chloride, 216; Determination of Cadmium as Sulphide, 332; Determination of Metallic Zinc in Zinc Dust, 458; Determination of Zinc in Silicious Ores Containing Lead . . . . .	458
Mintz, S. Determination of Free Hydrochloric Acid in Gastric Juice . . . . .	115
Moissan, Atomic Weight of Fluorine . . . . .	461
Mond, Langer and Quincke, Atomic Weight of Nickel . . . . .	464
Moore, R. W. Analysis of Marine Oil, 95; Comparative Results in the Analysis of Fats 104	104
Moraht. See Krüss.	
Morpurgo, J. Detection of Nitrobenzene in Oil of Bitter Almonds and Soaps . . . . .	465
Müller, J. A. Colorimetric Determination of Nitric Acid . . . . .	209
Müller, Max. Determination of Oxygen in Water . . . . .	78
Muter, J. Detection of Methylated Sweet Spirits of Nitre . . . . .	347
MYHLERTZ, FRED. G. Method for the Rapid Determination of Manganese in Slags and Ores . . . . .	267
Neumann, G. Separation of Zinc from Manganese . . . . .	69
Neumann, S. Determination of Quinine in Tannate of Quinine . . . . .	229
New Books . . . . .	116, 240, 468
Nickel, Atomic Weights of . . . . .	464
Nitrates, Colorimetric Methods for the Determination of in Potable Waters, 67; Determination of in Potable Waters, 208; Determination of Nitrogen in, 211; in Fertilizers, Determination of . . . . .	455
Nitric Acid, Apparatus for the Determination of, 188; Colorimetric Determination of, 209; Determination of Nitrogen in by Kjeldahl's Method . . . . .	224
Nitrites in Potable Waters, Estimation of . . . . .	455
Nitrobenzene, Detection of in Oil of Bitter Almonds and Soaps . . . . .	465
Nitrogen, Determination of, 77; Errors in the Determination of in Bodies Containing the Halogens, 88; Determination of in Urine, 109; Apparatus for the Determination of by Kjeldahl's Method, 179; Determination of in Nitrates, 211; Determination of in Nitric Acid by Kjeldahl's Method, 224; Determination in Tea, 443; Volumetric Determination of, 455; Estimation of in Chili Saltpeter . . . . .	456
Nitrogen and Zinc, Estimation of in Impregnated Railroad Ties . . . . .	457
Nitroso-Beta-Naphthol, Use for Separation of Iron from Manganese and Aluminum . . . . .	335
Nitrous Acid, Detection of . . . . .	81
Nitrous Oxide Formed in the Combustion of Organic Substances, Amount of . . . . .	97
<i>Note on Stilbite from York Haven, York County, Pa.</i> By C. H. Ehrenfeld . . . . .	157
<i>Note on the Relative Efficiency of the Solvents used in the Extraction of Fat from Milk Solids.</i> By H. Droop Richmond . . . . .	279
Notes . . . . .	119, 469
<i>Notes from the Laboratory of Smith College.</i> By J. T. Stoddard . . . . .	34
Noyes, Atomic Weight of Oxygen . . . . .	462
OBITUARY . . . . .	119, 469
Oddy, R. W., and J. B. Cohen. The Stability of Permanganate Solutions . . . . .	327
Oil Cake, Determination of Fat in Linseed . . . . .	97
Oils and Fats, Revision of Constants Employed in Analysis of . . . . .	347
Oil, Detection of Cotton-seed in Olive Oil, 90; Detection of Sesame in Olive Oil, 92; Analysis of Marine, 95; Test for Cotton-seed in Lard, 238; of Bitter Almonds, Detection of Nitrobenzene in . . . . .	465
Oils, Detection of Adulteration in Essential, 89; Estimation of Essential by Maumene's Test, 237; Reaction of Silver Nitrate on Vegetable . . . . .	239
<i>On the Determination of Available Phosphoric Acid in Fertilizers Containing Cotton-seed Meal.</i> By F. B. Dancy . . . . .	395
<i>On the Method of Estimation of the Fatty Bodies in Vegetable Organisms.</i> By Walter Maxwell . . . . .	392
<i>On the Occurrence of Boracic Acid as an Impurity in Caustic Alkalies.</i> By F. P. Venable and J. S. Callison . . . . .	197
Opium, Morphiometric Assay of . . . . .	465
Ores, Determination of Manganese in . . . . .	267
Organic Compounds, Rapid Estimation of Sulphur in, 90; Amount of Nitrous Oxide Found in the Combustion of, 97; Simultaneous Estimation of Carbon and Sulphur in 105	105

	PAGE.
Organic Liquids and Urine, Detection of Mercury in . . . . .	91
OSBORNE, T. B. Apparatus for Determining Nitric Acid . . . . .	188
OSBORNE, T. B. See Johnson, S. W.	
Ostersetzer, O. Apparatus for Determining Carbon Dioxide . . . . .	204
Oven for Heating Crucibles . . . . .	59
Owen, F. A. Determination of Indigotine . . . . .	103
Oxygen, The Use of in Quantitative Analysis, 57; Dissolved in Water, Schützenberger's Process for the Estimation of, 71; Determination of in Water, 78; Atomic Weight of, 106; Prepared from Peroxide of Hydrogen, 202; Dissolved in Water, A New Method for the Determination of, 205; Decomposition of Pyrites with, 222; Determi- nation of in Air, 457; Atomic Weight of . . . . .	462
PALLADIUM, Atomic Weight of . . . . .	106
Para-Nitrotoluene, Estimation of . . . . .	235
Partridge, Atomic Weight of Cadmium . . . . .	463
"Parts per Million" to "Grains per Gallon," Conversion of . . . . .	121
Pattison, J. Testing for Beef Stearin in Lard . . . . .	89
Pepsin Tests, Relative Value of Different . . . . .	115
Perkins, F. P. Test for Cotton-seed Oil in Lard . . . . .	238
Permanganate Solutions, Stability of . . . . .	327
Peroxide of Hydrogen in Preparing Oxygen with the Kipp Apparatus, The Use of . . . . .	202
Phenol, Estimation of Water in . . . . .	341
Phosphates, Estimation of Alumina and Oxide of Iron in, 69, 214; Estimation of Iron Oxide in . . . . .	215
Phosphododekamolybdic Acid, Analytical Studies on . . . . .	60
Phosphor-Tin, Determination of Phosphorus in . . . . .	83
Phosphoric Acid, Determination of Available in Fertilizers Containing Cotton-seed Meal, 395; Determination of in Wines, 86; Determination of in Basic Slags . . . . .	459
<i>Phosphorus in Pig-Iron, Steel and Iron Ore.</i> By Clemens Jones . . . . .	268
Phosphorus, Determination of in Phosphor-Tin, 83; The Götz Method for the Determi- nation of in Steel . . . . .	83
Pig-Iron, Phosphorus in . . . . .	268
Pinch-cock, Modified Form of . . . . .	34
<i>Pipette for Hydrofluoric Acid.</i> By G. P. Vanier . . . . .	48
Plants, Distribution of Boracic Acid in . . . . .	191
Poison of Diphtheria . . . . .	358
Poison in Bodies, Detection of . . . . .	288
Poisonous Products of Sapogenous Intestinal Bacteria . . . . .	358
Potash, Determination of in Soils, 322; Vanadium in Caustic . . . . .	201
Potassium Hydroxide and Carbon in Analysis of Minerals . . . . .	322
Precipitation, Some Observations on . . . . .	316
Prunier, M. L. Simultaneous Estimation of Carbon and Sulphur in Organic Substances <i>Preservation and Analysis of Sugar Solutions.</i> By Hubert Edson . . . . .	105
Preusser, J. A Substitute for the Calcium Chloride Tube in Ultimate Analysis, 58; De- termination of Tungsten in Rich Tungsten Alloys . . . . .	75
Ptomaine from Urine in a Case of "Mumps" . . . . .	351
Ptomaines, Recent Researches in . . . . .	109
Purification of Hydrofluoric Acid . . . . .	56
Pyrites, Analysis of, 220; Decomposition of with Oxygen . . . . .	222
Pyrolusite, Analysis of . . . . .	216
QUINCKE. See Mond.	
Quinine Alkaloids, Behavior of towards Xylene and Mayer's Reagent . . . . .	104
Quinine, Determination in Tannate of Quinine, 229; Rapid Estimation in Medicine . . . . .	238
RAFFINOSE AND SACCHAROSE, Simultaneous Estimation of . . . . .	349
<i>Rapid Determination of Bromine in Presence of Chlorine.</i> By Charles C. Hall . . . . .	167
Rathgen, E. Determination of Cane Sugar in Liquors, Confectionery and Chocolate . . . . .	98

	PAGE.
Raulin, J. Determination of Potash and Humus in Soils . . . . .	322
Reagent for Copper, Pretended . . . . .	217
Reagents, the Concentration of, 199; System of, Based on the Equivalents . . . . .	317
Reddrop, J. A System of Chemical Reagents Based on the Equivalents of the Elements . . . . .	317
Reinbach, E. Correction in Thermometer Readings for the Part of the Stem Outside the Vapor . . . . .	316
Rempel, R. Use of Normal Ammonia Solution . . . . .	204
<i>Report of the Committee on Methods of Sugar Analysis of the Louisiana Sugar Chemists' Association</i> . . . . .	I
Reverdin, F., and C. de la Harpe. Estimation of Para-Nitrotoluene . . . . .	235
Riban, J. Estimation of Zinc, 219; The Separation and Determination of Zinc in Presence of Iron and Manganese . . . . .	331
RICE, CHARLES. Coil for Milk Analysis . . . . .	155
Richardson, A. Arrangement for Sealing Tubes under Pressure . . . . .	311
RICHMOND, H. DROOP. Milk Analysis, 26, 241; Note on the Relative Efficiency of the Solvents used in the Extraction of Fat from Milk Solids . . . . .	279
Richmond, H. D. See Seaton, Dr.	
Rideal, S. Colorimetric Methods for the Determination of Nitrates in Potable Waters . . . . .	67
Roscoe, H. E., and Joseph Lunt. Schützenberger's Process for the Estimation of Dissolved Oxygen in Water . . . . .	71
Rose. See Warren, C. J. H.	
Ross, B. B. A Modified Method of Executing the Potassium Ferrocyanide Test in Glucose Determinations . . . . .	427
Rossi, A. J. Titanium in Blast Furnaces . . . . .	227
Röttger, H. Tests for Adulterants in Wax . . . . .	346
Roux and Chamberland. Recent Researches on Ptomaines . . . . .	109
 SACCHAROSE AND RAFFINOSE, Simultaneous Estimation of . . . . .	349
Saccharin, Detection of . . . . .	101
Saltpeter, Estimation of Nitrogen in . . . . .	456
Schaumann, H. Determination of Albumen in Urine . . . . .	109, 114
SCHNAIBLE, J. F. Analysis of Soaps . . . . .	147
Schmid, W. Determination of Fat in Milk . . . . .	102
Schmitt, T. F. Determination of Nitrates in Fertilizers . . . . .	455
Schultze, W. Estimation of Available Extract in Malt . . . . .	92
Schützenberger's Process for the Estimation of Dissolved Oxygen in Water . . . . .	71
Sealing Tubes under Pressure, Arrangement for . . . . .	311
Seaton, Dr., and H. D. Richmond. Rapid Estimation of Quinine in Medicine . . . . .	238
Sewage Decomposition in Streams . . . . .	39
SEYDA, DR. ANTON. Detection and Quantitative Estimation of Inorganic and Organic Poisons in Bodies . . . . .	288
Shaking Liquids, Apparatus for . . . . .	57
Silica in Silicates, Determination of . . . . .	159
Silicates, Analysis of . . . . .	63
Silicon on the Properties of Steel, Influence of . . . . .	84
Silver, Electro-Deposition of . . . . .	460
Silver Nitrate, Reaction on Vegetable Oils . . . . .	239
Silver Solution, Standardization of . . . . .	55
Sirups, Determination of the Specific Gravity of . . . . .	202
Slags, Determination of Manganese in, 267; Determination of Phosphoric Acid in Basic . . . . .	459
Soaps, Analysis of, 147; Detection of Nitrobenzene in . . . . .	465
Sodium Carbonate, An Investigation of . . . . .	202
Sodium Hydroxide and Carbon in Analysis of Minerals . . . . .	322
Soils, Determination of Potash and Humus in . . . . .	322
<i>Some Modifications of the Method for Determining Crude Fiber.</i> By W. A. Withers . . . . .	35
<i>Some Notes on the Determination of Sugars with Fehling's Solution.</i> By H. E. L. Horton . . . . .	370
<i>Some Points in the Determination of Silica in Silicates by Fusion with Alkaline Carbonates.</i> By James P. Gilbert, B. S. . . . .	159
Smith, E. F. Vanadium in Caustic Potash . . . . .	210



	PAGE
Smith, F. J. A Water Jacketed Flexible Tube . . . . .	55
Smith, J. H. Volumetric Determination of Nitrogen . . . . .	455
Smith, W. Bottinger's New Reaction for Tannic and Gallic Acids . . . . .	341
SNYDER, HARRY. The Determination of Theine in Tea by the Kjeldahl Nitrogen Method . . . . .	443
Specific Gravity of Sirups, Determination of the . . . . .	202
SPENCER, G. L. An Improved Method for the Estimation of Theine in Tea . . . . .	158, 390
Spirits, Furfural in . . . . .	466
Standard Solution of Ferric Salts, Preparation of without titration . . . . .	67
Standardization of Silver Solutions . . . . .	55
Stannous Chloride, Estimation of Free Hydrochloric Acid in . . . . .	216
Startthagen. See Baginsky.	
Stead, J. E. Determination of Aluminum in Iron and Steel . . . . .	225
Stearin in Lard, Testing for . . . . .	89
Stebbins, J. H. Relative Value of Pepsin Tests . . . . .	115
Steel, Influence of Silicon on the Properties of, 84; Determination of Aluminum in, 225, 337; Phosphorus in, 268; Sulphur in, 335; Carbon in . . . . .	403
Sterilization of River Water by Mine Water, The Alleged . . . . .	207
Stilbite from York County, Pa. . . . .	157
STILLMAN, THOS. B. The Composition of Boiler Scale, 24; The Analysis of Water to Determine Scale-Forming Ingredients . . . . .	446
STODDARD, J. T. Notes from the Laboratory of Smith College; A New Test Tube Holder; A Modified Form of Pinch-cock; Filtration under Pressure . . . . .	34
Stokes, A. W. Rapid Estimation of Fat in Milk . . . . .	89
Strontium Barium, and Calcium, Separation of . . . . .	76
<i>Study of a Method for the Quantitative Determination of Sucrose, Invert Sugar and Dextrose, or Levulose.</i> By F. G. Weichmann . . . . .	253
Stutzer, A. Apparatus for Shaking Liquids, 57; Estimation of Iron Oxide in Phosphates . . . . .	215
Substitute for Kipp's Apparatus . . . . .	54
Sucrose, Determination of . . . . .	253
Sugar, Report of the Committee of the Louisiana Sugar Chemists' Association on Methods of Analysis of, 1; Determination of in Liguers, Confectionery, and Chocolate, 98; Determination of Ash in, 102, 103; Detection of in Urine, 139; Determination of Invert, 253; Determination of with Fehling's Solution, 370; Solutions, Preservation and Analysis of, 381; Method for Obtaining Constant Ratio of Reduction of Copper with, 387; Estimation of Ash in by Incineration with Benzoic Acid . . . . .	467
Sulphides, Decomposition of with Bromine Vapor . . . . .	221
Sulphocyanide of Potash, Determination of Chlorine in . . . . .	223
Sulphur, Determination of in Coal, 83; Rapid Estimation of in Organic Compounds, 90; Simultaneous Estimation of with Carbon in Organic Compounds, 105; Wiborgh's Method for in Iron and Steel . . . . .	335
Sulphuretted Hydrogen Generator . . . . .	205
Sulphuric Acid, Volumetric Estimation of Combined . . . . .	73
"Sweet Spirits of Nitre," Detection of Methylated . . . . .	347
TANNIN, Estimation of by Potassium Permanganate, 93; Colorimetric Method for Estimating in Barks, 341; Volumetric Determination of . . . . .	342
Tannate of Quinine, Determination of Quinine in . . . . .	229
Tannic and Gallic Acids, Bottinger's New Reaction for . . . . .	341
Tartaric Acid in Vinegar, Determination of . . . . .	102
Tea, Estimation of Theine in, 158, 390; Theine in, Determination of . . . . .	443
Tellurium, Estimation and Separation . . . . .	319
Terbium and Gadolinium, Atomic Weights of . . . . .	463
Test Tube Holder, a New . . . . .	34
Theine in Tea, Estimation of, 158, 390; Determination . . . . .	443
<i>The Analysis of Soaps.</i> By J. F. Schnaible . . . . .	147
<i>The Analysis of Water to Determine Scale-Forming Ingredients.</i> By Prof. Thomas B. Stillman . . . . .	446
<i>The Composition of Boiler Scale.</i> By Thomas B. Stillman . . . . .	24
<i>The Determination of Theine in Tea by the Kjeldahl Nitrogen Method.</i> By Harry Snyder . . . . .	443

	PAGE.
<i>The Distribution of Boracic Acid Among Plants.</i> By J. S. Callison . . . . .	191
<i>The Filtration of Natural Waters.</i> By Thomas M. Drown . . . . .	428
<i>The Proper Standard for the Atomic Weights.</i> By F. P. Venable . . . . .	365
<i>The Sanitary Examination of Water as Practiced in the Hygienic Laboratory of the University of Michigan.</i> By V. C. Vaughan . . . . .	142
The Use of Oxygen in Quantitative Analysis . . . . .	57
Thermometer Readings, Correction in . . . . .	316
Thiocyanates, Gravimetric Determination of . . . . .	103
Thomson, E. A Substitute for Kipp's Apparatus . . . . .	54
Thomson, R. T., and H. Ballantyne. On the Revision of Constants Employed in the Analysis of Fats and Oils . . . . .	347
Thörner, W. Contributions to Gas Analysis . . . . .	58
The Estimation of Nitrites in Potable Waters . . . . .	455
Thresh, J. C. Determination of Oxygen Dissolved in Water . . . . .	205
Tin, Detection of in Minerals . . . . .	66
Tinned Meat, Analysis of . . . . .	338
Titanium in Blast Furnaces . . . . .	227
Titration Apparatus, A New . . . . .	198
Torrey, J. A Simple Form of Quick Filter . . . . .	315
Trillich, H. Estimation of Carbonic Acid in Drinking Water Containing Magnesia . . . . .	217
Tubes, Arrangement for Sealing under Pressure, 311; Graduation of for Gasometric Apparatus . . . . .	202
Tungstic and Vanadic Acids, Separation of . . . . .	222
Tungsten, Determination of in Metallic Tungsten, 67; Determination of in Rich Tungsten Alloys, 75; Analysis of . . . . .	227
Tungsten Steel, Analysis of . . . . .	227
<i>Two Methods for the Direct Determination of Chlorine in Mixtures of Alkaline Chlorides and Iodides.</i> By F. A. Gooch and F. W. Mar . . . . .	243
URINE, Detection of Mercury in, 91; Determination of Nitrogen in, 109; Determination of Albumen in, 109, 114; Detection of Sugar in . . . . .	139
VANADIC and Tungstic Acids, Separation of . . . . .	222
Vanadium in Caustic Potash . . . . .	201
VANIER, G. P. Pipette for Hydrofluoric Acid . . . . .	48
VAUGHAN, V. C. Sanitary Examination of Water at the University of Michigan . . . . .	142
VENABLE, F. P., AND J. S. CALLISON. Occurrence of Boracic Acid as an Impurity in Caustic Alkalies . . . . .	197
VENABLE, F. P. The Proper Standard for the Atomic Weights . . . . .	365
Vernon, H. M. Note on Water Analysis . . . . .	78
Venator. See Isbert.	
Vignon, L. Estimation of Dissolved Carbonic Acid . . . . .	77
Vinegar, Determination of Free Tartaric Acid in . . . . .	102
Volumetric Determination of Copper, 210, 319, 320; of Zinc and Copper, 212; of Acids, 218; of Combined Sulphuric Acid, 73; of Bromine in Presence of Chlorine and Iodine, 69; of Free Halogens and of Iodine in Presence of Chlorine and Bromine . . . . .	321
Voree. See Burton.	
Vosmaer, A. Method of Preparing Chromic Chloride . . . . .	59
WAINWRIGHT, J. H. Estimation of Commercial Glycerine . . . . .	96
Waller, E. Purification of Alcohol, 86; Determination of Lithia in Mineral Waters . . . . .	325
Walls, F. Milk Analysis . . . . .	337
Wanklyn, J. A. On the Determination of Oxygen in the Air . . . . .	457
Warder, R. B. Qualitative Tests for the Limit of Impurity in Chemicals of the U. S. Pharmacopoeia . . . . .	316
Warren, C. J. H., and C. L. Rose. The Analysis of Certain Samples of Tinned Meat . . . . .	338
Warren, H. N. Magnesium as a Reagent, 54; Method for Examination of Meat Extracts, 105; Brief Summary on Practical Manipulation, 203; Analysis of Copper and Zinc Alloys, 210; A New Appliance for the Detection of Combustible Gases when in Admixture with the Atmosphere . . . . .	313
Wash Bottles, A New Valve for . . . . .	141

	PAGE
Water, Determination of Total Residue in, 53; Analysis of, 64, 78, 142; Free from Ammonia, 71; Containing Magnesia, Estimation of Carbonic Acid in, 217; Determination of Iron in, 82; Determination of Chlorine in, 82; Determination of Dissolved Oxygen in, 205; The Alleged Sterilization of River, 207; Determination of Nitrates in Potable, 208; Estimation of in Phenol, 341; Filtration of Natural, 428; Determination of Scale-forming Ingredients, 446; Free and Combined Carbonic Acid in, 451; Estimation of Nitrites in Potable . . . . .	455
Water-Bath Regulator . . . . .	56
Water Jacketed Flexible Tube . . . . .	55
Waters of Excelsior Springs, The Manganese . . . . .	208
Watson, G. Some Observations on Precipitation . . . . .	316
Wax, Tests for Adulterants in . . . . .	346
Weeren. Atomic Weights of Manganese . . . . .	463
Weichmann, E. G. Determination of Ash in Raw Sugars . . . . .	103
WEICHMANN, F. G. Study of a Method for the Quantitative Determination of Sucrose, Invert Sugar and Dextrose, or Levulose . . . . .	253
Wein, E. Conversion Table for Fehling's Solution . . . . .	329
Wainwurm, S. Determination of Boric Acid in Wine . . . . .	102
Williams, R. Detection of Adulteration in Essential Oils, 89; Estimation of Fatty Acids in Alizarin Oil, 237; Maumene's Test for Essential Oils . . . . .	237
Williamson, R. J. See Haycraft, J. B.	
Wilson, J. A. Estimation of Water in Phenol . . . . .	341
Wine, Examination of and Determination of Phosphoric Acid in, 86; Method of Stating the Analysis of, 93; Determination of Boric Acid in . . . . .	102
WINTON, A. L. Apparatus for Drying in Hydrogen, 175; Aliquotimeter . . . . .	178
WITHERS, W. A. Determination of Crude Fiber . . . . .	35
Woodman, D. Note on Lead Poisoning by Carbonated Beverages . . . . .	353
XYLENE, Behavior of Quinine Alkaloids towards . . . . .	104
YOUNGER, W. Determination of Chlorine and Hydrochloric Acid in a Mixture of two Gases . . . . .	328
ZALOZIECKE, R. A New Indicator (Alpha-Naphthol Benzein) . . . . .	315
Ziegler, A. Analysis of Tungsten, 67, 227; of Ferro-Tungsten, Tungsten-Steel, Ferro-Chromium, and Chromium Steel . . . . .	227
Zsigmondy, R. Error in the Determination of Nitrogen in Bodies Containing the Halogens . . . . .	88
Zinc, Separation from Manganese, 69; and Copper Alloys, Analysis of, 210; Volumetric Determination, 212; Determination of Cadmium in, 213; Estimation of, 219; Separation and Determination in Presence of Iron and Manganese, 331; and Nitrogen, Estimation of in Impregnated Railroad Ties, 457; Determination of Metallic, in Zinc Dust, 458; Determination of in Silicious Ores Containing Lead . . . . .	458

1











